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# **Guidance Document: Surface Soils Sampling for Munition Residues in Military Live-Fire Training Ranges**

*Canadian Protocol*

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Isabelle Poulin  
Andre Marois  
Annie Gagnon*

**Defence R&D Canada – Valcartier**

Technical Report

DRDC Valcartier TR 2011-447

December 2012

**Canada**



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December 2012

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## Abstract

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This document represents a comprehensive site characterization guidance addressing the determination of the concentration of munitions constituents in military training range surface soils. It is based on more than 15 years of multidisciplinary research dedicated to the study of the source, dispersion, fate and transport of munitions constituents. Energetic residues and metals are heterogeneously distributed over military training ranges as particles of various sizes, shapes, and compositions. The sampling strategy was designed to address the compositional and distributional heterogeneities and to obtain representative mean soil concentrations in area where munitions constituents are expected, or decision units. The sample treatment, processing and analysis were also carefully studied and optimized. Most munitions constituents are deposited on the surface, with the highest measured concentrations at firing positions, near targets, at low-order or cracked UXO vicinity and where demolition activities are performed. This report summarizes the sampling strategies recommended for various types of ranges and covers the safety aspects related to sampling in UXO contaminated lands, the sampling equipment, sample processing and analysis. This protocol was developed during investigations on active ranges and primarily addresses potential surface source zones from which munitions residues could be migrating into surface and groundwater systems.

## Résumé

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Ce document est un guide détaillé de caractérisation des secteurs d'entraînement militaire ayant pour but de déterminer la concentration des résidus de munitions dans les sols de surface. Il est basé sur plus de 15 années de recherche pluridisciplinaire consacrée à l'étude de la source, la dispersion, le sort et le transport des constituants de munitions. Les résidus énergétiques et les métaux sont dispersés de façon hétérogène dans les secteurs d'entraînement militaire sous forme de particules de différentes tailles, formes et compositions. Les stratégies d'échantillonnage ont été développées pour répondre à l'hétérogénéité compositionnelle et de distributionnelle et afin de déterminer les concentrations moyennes de résidus dans les sols, à l'intérieur d'unités de décisions, soient les zones où la présence de résidus de munitions est suspectée. Le traitement, la préparation et l'analyse de l'échantillon ont été soigneusement étudiés et optimisés. La plupart des constituants des munitions sont déposés sur la surface, avec les concentrations les plus élevées retrouvées aux positions de tir, autour des cibles, à proximité et autour des munitions non éclatées ou craquées et aussi là où les activités de démolition sont effectuées. Ce rapport résume les stratégies d'échantillonnage recommandées pour les différents types de champs de tir et couvre les aspects de sécurité liés à l'échantillonnage dans des terrains contenant des munitions non éclatées, le matériel d'échantillonnage, le traitement des échantillons ainsi que l'analyse. Ce protocole a été développé au cours de caractérisations effectuées sur les secteurs d'entraînement actifs et traite principalement des sources potentielles dans les zones de surface à partir desquelles les résidus de munitions pourraient migrer vers les systèmes d'eau de surface et d'eau souterraine.

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## Executive summary

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### **Guidance Document: Surface Soils Sampling for Munitions Residues in Military Live Fire Training Ranges and Training Areas: Canadian Protocol**

**Thiboutot, S.; Ampleman, G.; Brochu, S.; Poulin, I.; Marois, A.; Gagnon, A.;  
DRDC Valcartier TR 2011-447; Defence R&D Canada – Valcartier; March 2012.**

**Introduction or background:** Research dedicated to the understanding of munitions environmental impacts in live firing range was initiated in the mid 90's. Range and training area (RTA) characterization for the determination of munitions constituent residues in the surface was done extensively both in Canada and in the United States. In parallel, deposition studies both at impact areas resulting from detonation processes and at firing positions resulting from propellant combustion processes contributed to the understanding of the source terms of contamination.

**Results:** The research dedicated to munitions deposition and fate led to the development of a detailed protocol for the effective and safe characterization of range and training areas. The distribution of munition constituents is widely heterogeneous, both in its distribution and composition. This mandated the application of multi increment soil sampling in judgmental decision units and a subsequent thorough sub-sample homogenization process. This protocol covers the main contaminants of concerns, propellants, explosives and metals.

**Significance:** The application of this protocol in any future RTA surface soil characterization will ensure that scientifically defensible representative results will be obtained and it will minimize the associated sampling and analysis costs. Areas of concerns will be identified and whenever appropriate, remediation can be applied to avoid a further dispersion and movement of the identified contaminants. Environmental officers will be able to write statement of work in order for contractors to apply the DRDC protocol in their respective RTAs.

**Future plans:** DRDC will continue to support the Department of National Defence land owners in any future RTA characterization, whenever complementary guidance or expertise is needed. In parallel, mitigation methods are being studied to minimize the adverse impacts that were observed over the years. As an example, a burning table was developed and fielded to replace the field expedient burning of excess artillery propellants. Also, an in situ burning of surface propellant residues in firing position is under development and other efforts, including the development of future greener munitions, are ongoing.

## Sommaire

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### **Guidance Document: Surface Soils Sampling for Munitions Residues in Military Live Fire Training Ranges and Training Areas: Canadian Protocol**

**Thiboutot, S.; Ampleman, G.; Brochu, S.; Poulin, I.; Marois, A.; Gagnon, A.; DRDC Valcartier TR 2011-447; R & D pour la défense Canada – Valcartier; Mars 2012.**

**Introduction ou contexte:** La recherche dédiée à la compréhension des impacts environnementaux du tir réel de munitions a été lancée au milieu des années 90. La caractérisation des aires d'entraînement militaire pour déterminer les résidus de munitions dispersés à la surface a été faite abondamment au Canada et aux États-Unis. En parallèle, des études de déposition tant au niveau des zones d'impact résultant des processus de détonation et aux positions de tir résultant des processus de combustion ont contribué à la compréhension des sources de contamination.

**Résultats:** La recherche dédiée à la déposition de résidus de munitions et à leur devenir a conduit à l'élaboration d'un protocole détaillé pour la caractérisation efficace et sûre des zones d'entraînement. La dispersion des constituants de munition est très hétérogène, tant dans sa répartition que dans sa composition. Ceci a nécessité l'application d'un échantillonnage multi incrémenté du sol dans les unités de décision de jugement et un processus rigoureux d'homogénéisation ultérieure du sous-échantillon. Ce protocole couvre les principaux contaminants des propulsifs, des explosifs et des métaux qui nous préoccupent.

**Importance:** L'application de ce protocole dans toutes caractérisations futures des sols de surface fera en sorte que des résultats représentatifs scientifiquement défendables seront obtenus et ceci minimisera l'échantillonnage et les coûts d'analyse. Les zones à risques seront identifiées et lorsque nécessaire, des techniques d'assainissement pourront être appliquées pour éviter une nouvelle dispersion et le mouvement des contaminants identifiés. Les officiers d'environnement seront en mesure d'écrire des énoncés de travail pour que les entrepreneurs puissent appliquer le protocole de RDDC dans leur secteur d'entraînement respectif.

**Perspectives:** RDDC continuera de soutenir le Ministère de la Défense Nationale dans toutes caractérisations futures, chaque fois que des conseils complémentaires ou une expertise particulière sera nécessaire. En parallèle, des méthodes d'atténuation sont présentement étudiées pour minimiser les impacts négatifs qui ont été observés au cours des années. À titre d'exemple, une table de combustion a été développée et mise en service pour disposer des excès de poudres à canon provenant des exercices d'artillerie. Également, le brûlage in situ des résidus de propulsifs à la surface des positions de tir est en cours de développement ainsi que d'autres efforts, y compris le développement de munitions vertes du futur, qui sont en cours



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# Table of contents

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Abstract .....	i
Résumé .....	i
Executive summary .....	iii
Sommaire .....	iv
Table of contents .....	vi
List of figures .....	viii
List of tables .....	x
Acknowledgements .....	xi
1 Introduction.....	1
2 Contaminants of concern .....	4
2.1 Energetic materials .....	4
2.1.1 Definitions.....	4
2.1.2 Source of EM in RTAs.....	7
2.1.2.1 Firing positions .....	7
2.1.2.2 Target impact area .....	14
2.2 Metals .....	22
2.2.1 Sources of metals in RTAs.....	22
2.2.1.1 Firing positions .....	23
2.2.1.2 Target area .....	24
2.3 Fate and transport .....	25
2.3.1 Energetic materials : explosives and propellant.....	26
2.3.2 Metals.....	28
2.4 MC environmental and health related thresholds .....	29
2.4.1 Explosives and propellants.....	29
2.4.2 Metals.....	33
3 Characterization approach .....	34
3.1 General sampling strategy to control heterogeneity .....	34
3.1.1 DU for risk-based human health soil screening levels .....	40
3.1.2 DU for protection of surface and groundwater .....	40
3.1.3 DU for risk-based ecological soil screening levels .....	40
3.2 Actual and historical records review .....	40
3.3 Safety aspects/sampling in UXO contaminated sites .....	41
3.4 Soil sampling.....	42
3.4.1 Soil sampling equipment.....	42
3.4.1.1 Subsurface sampling.....	45
3.5 Sample processing and storage.....	45

3.5.1	Sample storage and maximum holding times .....	46
3.5.2	Energetic materials processing.....	46
3.5.2.1	Air-drying .....	46
3.5.2.2	Acetone slurry.....	49
3.5.2.3	Grinding procedure.....	51
3.5.2.4	Comparison of the two homogenization methods – recuperation study.....	55
3.5.2.5	Sub-sampling homogenized samples.....	56
3.5.2.6	Extraction of the sub-sample of homogenized soil.....	57
3.5.3	Metals processing.....	57
3.6	Sample analysis .....	58
3.6.1	EM.....	58
3.6.2	Metals.....	62
3.6.2.1	Extraction of metals.....	62
3.6.2.2	Chemical analysis.....	63
3.7	Quality assurance/Quality control .....	64
3.8	Requirements for contract laboratories.....	65
3.8.1	EM.....	65
3.8.2	Metals.....	65
4	Specific strategies designed for ranges.....	67
4.1	Grenade ranges .....	68
4.2	Antitank ranges.....	71
4.3	Small arms ranges.....	74
4.3.1	Sampling strategy for a hypothetical 12-lane backstop berm .....	75
4.3.2	Analysis.....	77
4.4	Artillery, mortar ranges, air-soil bombing ranges and battleruns .....	78
4.5	Demolition ranges .....	81
4.6	Wide area assessment.....	82
5	Conclusion .....	84
	References .....	86
	Annex A .. Soil sampling equipment .....	101
	Annex B... Metal analytes and detection limits .....	102
	Annex C... Generic statement of work.....	103
	List of symbols/abbreviations/acronyms/initialisms .....	105

## List of figures

---

Figure 1. RTAs Characterized in North-America. ....	2
Figure 2. Major classes of Energetic Materials. ....	5
Figure 3. Propellant deposition trial – 7.62 mm. ....	8
Figure 4. Propellant deposition trial – 105 mm artillery. ....	8
Figure 5. Propellant deposition trial – 105 mm tank. ....	9
Figure 6. 105 gun propellant residues on witness plate. ....	9
Figure 7. Close view of an NC-based propellant fibre embedded with 2,4-DNT after reaction with Griess reagent. ....	10
Figure 8. Field expedient burning of excess artillery propellants. ....	12
Figure 9. Left over residues after burning on snow. ....	13
Figure 10. Schematic of the Canadian excess artillery propellant burn table. ....	14
Figure 11. High-order detonation on snow profile. ....	15
Figure 12. Collection of residues from high-order detonation on snow. ....	15
Figure 13. Comp B particles from low-order detonation of a 81-mm mortar. ....	17
Figure 14. Low order detonation artillery crater in Gagetown RTA. ....	18
Figure 15. Low order detonation crater in Cold Lake RTA. ....	18
Figure 16. Set up to study the cracking of UXOs using a donor round. ....	20
Figure 17. Resulting cracked UXO. ....	20
Figure 18. Cracked rounds found in an RTA. ....	21
Figure 19. Corrosion study ongoing at CFB Petawawa. ....	22
Figure 20. Conceptual model for the environmental fate of MC. ....	26
Figure 21. Sampling pattern for optimizing sample representativeness in a square or rectangular pattern. ....	38
Figure 22. Sampling pattern for optimizing sample representativeness in a circular pattern. ....	38
Figure 23. Metal detector for proofing prior to sub-surface sampling. ....	42
Figure 24. Soil sampling metallic spoon. ....	43
Figure 25. Soil sampling corer. ....	44
Figure 26. Sample transferred in a glass vessel for drying. ....	47
Figure 27. Soil samples drying on a lined metal sheet and multiple samples drying in a ventilated plastic box. ....	48
Figure 28. Samples under a hood for drying. ....	48

Figure 29. Acetone slurry.....	49
Figure 30. Sieving and storing the dried sample. ....	50
Figure 31. Breaking of the NC crust with a mortar and pestle before sieving. ....	51
Figure 32. Material needed for sieving before grinding. ....	52
Figure 33. Sieving of dried soil with a #10 sieve. ....	52
Figure 34. Left: coarse fraction in the plastic bag, fine fraction in the bowl; Right: sieved fractions ready for identification and storage.....	53
Figure 35. LabTech Essa LM-2 Ring mill, opened and closed. ....	54
Figure 36. Insertion of the bowl in the pneumatic clamp.....	54
Figure 37. Grinding steps: Empty dish and puck; puck on top of soil sample before grinding; removing the puck after grinding; ground soil.....	55
Figure 38. Build-up of a 10-g sub-sample using a systematic approach (30-increment). ....	56
Figure 39. Chromatogram for a 25 ppm calibration solution of mixed EM, detection at 250 nm.....	60
Figure 40. Typical grenade range.....	69
Figure 41. Low order hand grenade.....	70
Figure 42. Suggested DUs within a grenade impact area.....	70
Figure 43. Typical antitank ranges and close view of a target tank. ....	72
Figure 44. Suggested DU for an antitank target. ....	73
Figure 45. Suggested DUs for an antitank firing position. ....	73
Figure 46. Typical sampling strategies for a SAR FP. ....	74
Figure 47. Sampling pattern for a 12-lane backstop berm.....	76
Figure 48. Illustration of an artillery firing range.....	79
Figure 49. Suggested DU for an air-to-ground target.....	80
Figure 50. Proposed DUs for artillery/mortar impact areas or battle runs. ....	80
Figure 51. Suggested DU in the firing position of artillery guns. ....	81
Figure 52. Representative detonation bays and wood cutting area. ....	82

## List of tables

---

Table 1. Physical and chemical properties of nitroaromatics, nitramines and nitrate esters. ....	5
Table 2. Explosives formulations. ....	6
Table 3. Propellant formulations. ....	7
Table 4. Deposition of propellant residues from live-firing of various platforms.....	11
Table 5. Mass of explosive deposited from high order detonations. ....	16
Table 6. Mass of explosive deposited from low order detonations. ....	17
Table 7. Constituents of small arms munitions (reproduced from [134]) .....	25
Table 8. Military soil quality guidelines for EM .....	30
Table 9. Environmental quality guidelines for EM in U.S. EPA regions 3, 6 and 9. ....	31
Table 10. Environmental quality guidelines for EM in British Columbia.....	32
Table 11. Environmental quality guidelines for 2,4-DNT in Ontario. ....	33
Table 12. Environmental quality guidelines for EM in Quebec. ....	33
Table 13. Minimum number of increments recommended in function of the size of the DU.....	36
Table 14. Pulverisation contaminants added by grinding equipment.....	58
Table 15. Analytes detected with EPA Method 8330b.....	59
Table 16: Retention time and detection wavelength for analytes detected by HPLC (DRDC's HPLC system). ....	61
Table 17. EM commonly observed by Range type .....	67
Table 18. Metals commonly observed by Range type.....	68
Table 19. Detection limits (d) for metals by in soil and in water by Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS), and CCME Industrial Soil Quality Guidelines (ISQG). ....	102

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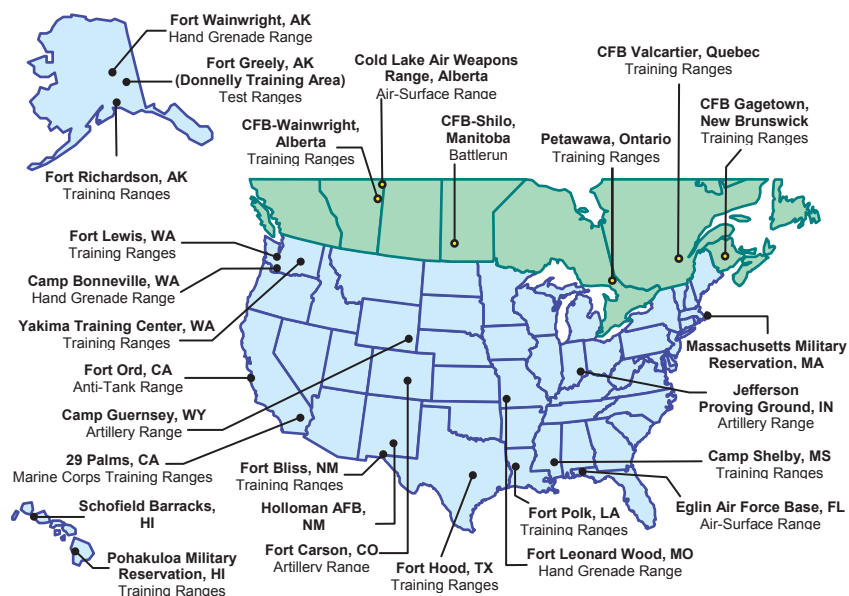


# 1 Introduction

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Live fire training on military Ranges and Training Areas (RTAs) is a critical component of combat readiness of our armed forces. The environmental impacts of munitions-related activities may threaten the accessibility and sustainability of RTAs. The Canadian sustainable military training R&D program, in agreement with the Sustainable Development Strategy promulgated by the Department of National Defence (DND) [1], is aimed at maintaining both military readiness and environmentally-friendly defence activities in order to ensure the long-term usage of military training areas. Moreover, as many other countries, Canada has to deal with growing public concerns and is facing more stringent environmental laws. Indeed, the Fisheries Act [2] prohibits *any work or undertaking that could result in the harmful alteration, disruption or destruction of the fish habitat* by introducing deleterious substances in water, while the Canadian Environmental Protection Act [3] is concerned with pollution prevention and toxic substances releases. Several compounds commonly found in military training areas, or munitions constituents (MC), are regulated by the Canadian Council of Ministers of the Environment (CCME) guidelines [4]. Some of these compounds are also on the list of priority substances of the ARET program (Accelerated Reduction/Elimination of Toxics) that promulgates the voluntary reduction or near-elimination of the release of some of the most persistent, bio-accumulative and toxic substances in the environment [5]. The United States (U.S.) Department of Defence (DoD), together with the Environmental Council of the States (ECOS) Sustainability Working Group and the Environmental Protection Agency (EPA), are also monitoring very closely some emerging contaminants on military sites [6].

Research dedicated to the understanding of munitions environmental impacts in live firing range was initiated in the mid 90's. In order to tackle the various aspects related to MC dispersion and fate, multidisciplinary collaborations were established with national and international research centers. In Canada, our main collaborators are the Institut national de la recherche scientifique – Centre Eau, Terre et Environnement (INRS-ETE) and the Biotechnology Research Institute (BRI), while in the United States (U.S.), it is the U.S. Army Engineer Research and Development Center (ERDC) Cold Regions Research and Engineering Laboratory (CRREL). Over the years, the various aspects of research were supported by many stakeholders, including DRDC R&D thrusts (Munitions and Firepower and Sustain thrusts), Director General Environment (DGE), Director Land Environment (DLE) and a U.S. peer reviewed funding program, the Strategic Environmental Research and Development Programme (SERDP, Arlington, VA). More specifically, Defence R&D Canada – Valcartier (DRDC Valcartier) was tasked by DLE at the end of the 90's to initiate a research program for the environmental assessment of the Army's RTAs. The RTA characterization work was conducted both in Canada and the United States and done in collaboration with U.S. scientists from ERDC-CRREL to better understand the nature and extent of contamination [7] - [38]. Figure 1 illustrates the numerous RTAs characterized for MC deposition across North America by the DRDC and U.S. ERDC teams. Note the various climates and geologies that have been studied. A tremendous amount of data from the Canadian's Army RTAs was obtained and a DLE report was published by Dr. Dana Pantea to collate all the information gathered over the years [38]. Dr. Pantea's report will be most helpful in any future RTA characterization, as it can give an estimate of the range of concentrations of MC that can be expected in specific types of ranges.



*Figure 1. RTAs Characterized in North-America.*

In 2000, a six-year research project (ER-1155) was initiated by DRDC and CRREL, co-sponsored by Canadian stakeholders and SERDP to study the deposition, accumulation, and fate of explosives at live-fire training ranges. SERDP project ER-1155 was focussed on impact areas where explosives such as cyclo-1,3,5-trimethylene-2,4,6-trinitramine (RDX) were deposited and thus where the potential for groundwater (GW) contamination was the highest. A significant portion of this work was performed in Canadian RTAs. The SERDP project ER-1155 allowed the development of transport processes descriptors for the current explosives and their main transformation products and contributed to the understanding of the various sources of explosive contamination in target impacts areas [40] -[46].

In 2006, project ER-1481 was initiated and co-sponsored by SERDP and DLE to study the distribution, fate and transport of propellant residues at firing points associated with live-fire training with munitions [47] - [61]. This allowed a better understanding of the contamination pattern at the firing positions, which was not suspected in the earlier years of the project. Both SERDP projects 1155 and 1481 linked the munitions usages in live fire training context with munitions residues found in soils at the military installations.

Several studies have also been performed on the wider fate of munitions constituents mostly in collaboration with INRS-ETE and BRI [62] - [75] and on the study of the ecotoxicological impacts of MC [76] - [80]. In 2004, DGE mandated BRI for the calculation of military-based quality guidelines for the main energetic residues [81]. They published their final report in 2006, and a revision of the criteria is presently ongoing.

Going back to RTA's characterization, over the years, various versions of protocols for the characterization of RTAs were published by DRDC, CRREL and under the auspices of The Technical Cooperation Programme (TTCP) [82] - [84]. More recently, CRREL published updated

versions of the U.S. protocol for the sampling for munitions constituents and sample homogenization and they influenced the modification of the U.S. EPA method SW-846 8330 used for the analysis of energetic materials, to method EPA SW-846 8330b that now includes sampling and processing methods [85] - [88]. Through DRDC's participation to the North Atlantic Treaty Organization (NATO), the authors are aware that very few countries have published such protocols up to now. The only country other than Canada or U.S. that has published a similar document is Norway [89]. Finally, the Unexploded Ordnances (UXO) Legacy Program recently tasked SAIC Canada for the development of an environmental site sampling protocol for UXO legacy sites. SAIC Canada conducted a literature review, contacted U.S. scientists and DRDC scientists and published a protocol in 2009 [90].

The goal of this current document is to provide the reader with a Canadian updated protocol to perform thorough RTA's characterization that will allow appropriate risk assessments. Some of the information will be complementary to the information available in the U.S. equivalent documents, while part of the information related to homogenization and metals dispersion and characterization is unique to this document. It will attempt to describe all aspects related to the source, dispersion, sampling, extraction and analysis of MC, while covering occupational health and safety issues when characterizing these particular sites. An overview of the associated background information on the main contaminants commonly found in RTAs, as well as some information on their fate and behaviour in the environment is also provided. Readers interested in more detailed information are invited to consult the numerous references provided in each section. The 2011 Canadian protocol is also intended to provide RTA's environmental officers with the knowledge to develop statements of work and review site-specific sampling plans and to provide consultants with guidance and source reference materials to develop scientifically sound site-specific sampling plans and cost estimates. This document addresses only surface soils, while a similar document will be published later on by INRS-ETE on the characterization of surface water and groundwater on active RTAs.

## 2 Contaminants of concern

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Accurately detecting the type and quantity of contamination of MC and their breakdown products in water, soil and sediment is vital to assessing the extent of contamination and ultimately the risk to human and ecological receptors. Several industry standard environmental site sampling protocols are available for common industrial/commercial contaminants. The protocol described in this document focuses on specific munitions related contaminants and methods specific to RTAs and Unexploded Ordnances (UXO) contaminated sites and assumes that the reader is familiar with standard sampling methods, procedures, tools and analysis and provides guidance built on this background. The contaminants of concern that might be dispersed in the environment following live fire training are mainly energetic materials and metals. Both organic and inorganic contaminants will be covered in this document.

### 2.1 Energetic materials

Both the propulsion and detonation of munitions in live fire training involves energetic materials. Section 2.1 will define the main energetic materials (EM), present the formulations used in conventional weapons and describe the identified source of MC in RTA's.

#### 2.1.1 Definitions

Conventional weapons use EM in the form of propellants and main charge explosives. A brief description of each type of EM is given below.

Explosives are classified as 'primary' or 'secondary' based on their susceptibility to initiation. Primary explosives, which include lead azide, lead styphnate, and mercury fulminate, are highly susceptible to ignition and are often referred to as initiating explosives, since they can be used to ignite secondary explosives. They are involved in the detonation initiation process, but a smaller amount is needed versus secondary explosives. Secondary explosives are much more prevalent on military sites than primary explosives. They include trinitrotoluene (TNT), hexahydro 1,3,5 trinitro-1,3,5 triazine (RDX), or high melting explosive octrahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and 2,4,6-trinitro-phenylmethylnitramine (tetryl). It has to be noted that tetryl has never been detected in Canadian RTAs so it will not be covered in this document. Since they are formulated to detonate under specific circumstances, secondary explosives are often used as main charges or boosting explosives. There are many ways to classify secondary explosives. First, they can fall into one of two main categories: (1) melt-cast explosives, based primarily on TNT, or (2) polymer-bonded explosives (PBX), which consist of a polymer matrix filled with a crystalline explosive such as RDX. Most of the actual stockpile of munitions is still based on melt cast formulations. Secondary explosives can also be classified according to their chemical structure. For example, TNT and trinitrobenzene are classified as nitroaromatics, nitroglycerine (NG) as nitrate ester whereas RDX and HMX are nitramines. The major classes of EM used by DND are presented in Figure 2 and their physico-chemical properties are presented in Table 1.

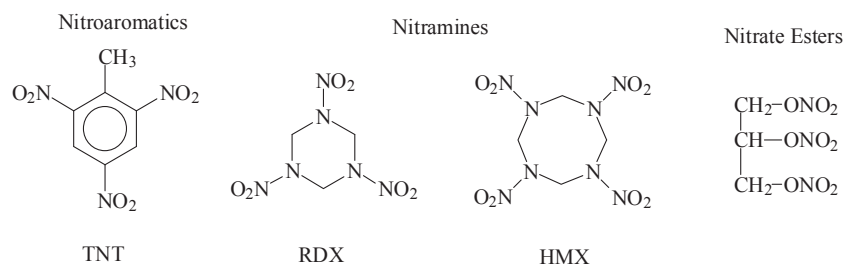


Figure 2. Major classes of Energetic Materials.

Table 1. Physical and chemical properties of nitroaromatics, nitramines and nitrate esters.

Analyte	Molecular <u>weight</u> (g)	Melting <u>point</u> (°C)	<u>Boiling point</u> (°C)	Water <u>solubility</u> (mg/L)	Vapor pressure <u>at</u> <u>20°C</u> (mm Hg)
TNT	227.13	80.1-80.6	240 (explodes)	130 (20°C)	$1.1 \times 10^{-6}$
RDX	222.26	204.1	dec.	42 (20°C)	$4.0 \times 10^{-9}$
HMX	296.16	276-280	dec.	5 (25°C)	$3.3 \times 10^{-14}$
TNB	213.11	122.5	315	34 (20°C)	$2.2 \times 10^{-14}$
DNB	168.11	89.6	300-303	460 (15°C)	$3.9 \times 10^{-3}$
2,4-DNT	182.15	71	300 (dec.)	270 (22°C)	$1.5 \times 10^{-4}$
2,6-DNT	182.15	64-66	285 (dec.)	206 (25°C)	$5.6 \times 10^{-9}$
2-ADNT	197.17	176	nd	2,800 (20°C)	$4 \times 10^{-5}$
4-ADNT	197.17	171	nd	2,800 (20°C)	$2 \times 10^{-5}$
NC	$10^5 - 10^6$	206	Dec.	Nil	nd
NG	227.1	14	50-60	1800 (25°C)	$2.0 \times 10^{-4}$

nd. Not determined, dec. Decomposes, TNB=trinitrobenzene, DNB=dinitrobenzene, DNT=dinitrotoluene, ADNT=aminodinitrotoluene, NC= nitrocellulose, NG= nitroglycerine

Propellants include both rocket and gun propellants. Most rocket propellants consist of a rubbery binder filled with ammonium perchlorate (AP) oxidizer and may contain powdered aluminum as fuel. Propellants may also be based on nitrate esters, usually nitroglycerine (NG), nitrocellulose (NC), or a nitramine such as RDX or HMX. Gun propellants are usually referred as single base (NC), double base (NC and NG), or triple base (NC and NG and nitroguanidine (NQ)). Single base propellants may also contain 2,4-dinitrotoluene (2,4-DNT). The vast majority of propellant formulations in Canada are either single or double base propellants. NC is prone to chemical and thermal degradation which may end-up in self-ignition. When used in propellants, degradation may negatively affect the propellant strength and other important ballistic properties. The degradation of NC leads to substances which speed up the degradation process, or else an autocatalytic reaction. To counteract this, stabilizers are added to the formulations. They react with these substances hereby delaying the degradation process. Diphenylamine (DPA) and ethyl centralite (EC) are the two mostly used stabilizers in propellant formulations. Table 2 and 3 present the most commonly used explosive and propellant formulations in North American's RTAs.

*Table 2. Explosives formulations.*

<b>Military appellation</b>	<b>Usage</b>	<b>Ingredients</b>
Composition B	Artillery, mortar, grenade	60% RDX (contains 10% HMX) 39 % TNT (1% TNT isomers and DNT)
C4	Demolition explosive	91 % RDX and wax
Tritonal	Air force bombs	80 % TNT 20 % aluminium
TNT	Artillery	TNT
Octol	Antitank rockets	70 % HMX (contains 10% RDX) 30 % TNT
A4	40-mm grenade	RDX (contains 10% HMX)

*Table 3. Propellant formulations.*

<b>Military appellation</b>	<b>Usage</b>	<b>Ingredients</b>
Single base	Small arms to 155-mm	NC, 2,4-DNT, DPA
Double base	Antitank, rockets	NC, NG, EC
Triple base	Large caliber guns	NC, NG, NQ, EC
Composite	Rockets and missiles	Polymeric binder, AP

## **2.1.2 Source of EM in RTAs**

An understanding of the source of MC in RTAs will facilitate the delineation of the decision units where sampling shall be conducted. The information presented in subsection 2.1.2 presents the conclusions drawn from major RTA characterization and from propellant and explosive deposition studies.

### **2.1.2.1 Firing positions**

Several environmental assessment studies have shown that residues coming from the incomplete combustion of gun propellant accumulate as solid fibrous particulates in front of the firing positions (FP) of guns, from small arms to large calibers. Figure 3 to Figure 6 present representative pictures of the trials conducted to monitor the deposition rate of propellant residues from the live firing of small arms, artillery, and tank munitions. Figure 6 presents a picture of a deposition witness plates where propellant particles accumulated upon firing of 105-mm artillery Howitzer guns, while Figure 7 presents a close view of the NC fibrous material that is deposited in the environment from the gun mouth. Antitank live firing is peculiar, as propellant residues are deposited both in front of the guns and behind the firing positions, in the back blast area of the shoulder-launched rockets.





*Figure 3. Propellant deposition trial – 7.62 mm.*



*Figure 4. Propellant deposition trial – 105 mm artillery.*





*Figure 5. Propellant deposition trial – 105 mm tank.*



*Figure 6. 105 gun propellant residues on witness plate.*



*Figure 7. Close view of an NC-based propellant fibre embedded with 2,4-DNT after reaction with Griess reagent.*

Constituents of concern are 2,4-DNT and NG, which are part of single and double base propellant, respectively. Concentrations up to 2 and 140 mg/kg were observed at the firing points (FP) of small arms ranges for 2,4-DNT and NG, respectively, while concentrations as high as 6100 mg/kg of NG were detected behind antitank firing positions [39]. The firing of a weapon also produces an aerial plume composed of various gases and particles.

Previous work was conducted in the United States by the U.S. Army Environmental Center to develop emission factors based on firing point emissions for various types of range operation, such as weapons firing, smoke and pyrotechnic devices, and exploding ordnances. The work, conducted with the EPA, used different munitions test facilities, such as test chambers, blast spheres and bang-boxes at the Aberdeen Test Center, Maryland, to sample and analyze emitted products. The results of these tests led to the calculation of emission factors that were published in the U.S. EPA Compilation of Air Pollutant Emission Factors (AP-42) [91]. The airborne emissions will not be covered in this report, however an interested reader can refer to the literature published on trials that were dedicated to the measurements of air emissions from live fire training in Canada with various calibers [50][51][54][55][56].

Two comparative studies [58], [60] on small arms live-firing indicated that the percentage of unburned NG per round varied between 0.001% and 5.32%, and that up to 2.1 mg of NG per round was deposited. This makes the burning efficiency of most small arms better than mortars, but worse than some artillery rounds. Although the amount of dispersed NG per round seems low, the large amount of small caliber ammunition fired in military training as compared to larger caliber ammunition can lead to the rapid accumulation of contaminants on the surface of the soil of small arms firing positions. Moreover, the small arms residues accumulate in a much smaller area than those of larger caliber ammunitions, leading to a higher concentration build-up. The measurement of the deposition rate of propellant residues from various platforms have resulted in

a good estimation of the source term of each type of firing and global results obtained are presented in Table 4.

*Table 4. Deposition of propellant residues from live-firing of various platforms.*

<i>Weapon system</i>	<i>Weapon size</i>	<i>Munition tested</i>	<i>EM</i>	<i>EM mass / round (g)</i>	<i>Residues / round (mg)</i>	<i>Deposition rates (%)</i>
<b>Small Cal.</b>	9-mm Pistol	M882	NG	0.0395	2.1	5.32
	5.56-mm Rifle	M855	NG	0.1640	1.8	1.10
	5.56-mm MG	M27	NG	0.1835	1.3	0.71
	7.62-mm MG	M80	NG	0.2670	1.5	0.56
			DNT	0.0037	0.0018	0.05
	12.7-mm MG	M9	NG	1.4960	11	0.74
<b>Small Cal. Canada</b>	9-mm Pistol	MK1 Ball	NG	0.0533	0.74	1.39
	9-mm Pistol	Frangible	NG	0.0482	0.95	1.97
	9-mm Pistol	115 FMJ Ball	NG	0.0521	2.03	3.90
	5.56-mm C7 Rifle	Frangible	NG	0.1710	1.06	0.62
	5.56-mm C7 Rifle	C77 ball clip	NG	0.1530	0.30	0.19
	5.56-mm C7 Rifle	C79A1 blank clip	NG	0.0761	0.02	0.05
	5.56-mm C8 AC	C77 ball clip	NG	0.1530	0.07	0.04
	5.56-mm C8 AC	C79A1 blank clip	NG	0.0384	0.02	0.06
	5.56-mm C9 MG	C77/C78 link	NG	0.1530	0.05	0.03
	5.56-mm C9 MG	C79A1 blank clip	NG	0.0761	0.01	0.01
	7.62-mm C6 MG	C21/C19 ball link	NG	0.0710	0.98	1.36
	7.62-mm C6 MG	C24 blank	NG	na	0.16	na
	0.338 Cal Rifle	Match B406	NG	0.5640	0.03	0.001
	0.5 Cal MG	M2/M17 link	NG	1.2620	0.25	0.02
	0.5 Cal Rifle	AAA750	NG	1.3500	0.27	0.02
<b>Med Cal.</b>	40 mm	Mk281 Mod 0	NG	0.37	2.2	0.59
		M430	NG	0.90	76	8.44
<b>Mortars</b>	60 mm	M888 / M702	NG	1.4	0.088	0.0065
	81 mm	M301A3 / M185	NG	30	1,000	3.3
	120 mm	M933 / M230	NG	25	350	1.4
<b>Rockets</b>	84 mm	M136 (AT4)	NG	130	95,000	73
	84 mm	Carl Gustav	NG	140	20,000	14
	66 mm	M72 LAW	NG	22	42	0.19
	204 mm	GMLRS	AP	57,400	<1.6	<0.000003
	203 mm	MK-58 AIM-7	AP	47,000	2.000	0.00000425
<b>Howitzers</b>	105 mm	M1 / M67	DNT	42	34	0.081
	105 mm	M1 charge 5	DNT	58	29	0.050
	105 mm	M1 charge 4	DNT	47	135	0.290
	105 mm	M1 charge 6	DNT	84	193	0.230
	155 mm	M107 / M3	DNT	2,500	1.2	0.0000480
	155 mm	L8 charge 3	NQ	761	0.066	0.00000870
<b>British L131</b>		L8 charge 5	NQ	1,938	0.857	0.0000442
		L10 charge 8	NQ	6,703	0.415	0.0000062
		L8 charge 3	NG	259	0.015	0.00000579
		L8 charge 5	NG	659	0.200	0.0000304
		L10 charge 8	NG	2,279	0	0
<b>Tank</b>	105-mm	C109A1(Canada)	DNT	300	7.9	0.00263

Accumulation of NG and 2,4-DNT in the environment is cumulative over the years, and probably even decades, as the NC matrix protects MC from degradation and dissolution processes. A study

on the fate of propellant residues was conducted on a former antitank firing position that had been inactive for more than 25 years [62]. This study demonstrated that levels as high as 4000 mg/kg of NG are still detected in the surface soils. The same conclusions were drawn by U.S. scientists Dontsova and Pennington [92].

Using Table 4 and data from range firing log book, it is now possible to estimate the quantity of propellant residues that was deposited in the last years in a specific range. As an example, if 100 rounds of 84 mm Carl Gustav have been fired on a range, it means that 200g of NG have been deposited behind the firing position. It can be a great tool in sampling design and estimation of the source of contaminant that has accumulated at a given location.

Up to early 2011, the burning of excess artillery propellant charges represented another source of propellant residues in RTAs. Artillery guns use a propelling charge system composed of multiple charge bags to fire projectiles at required distances. The number of charge bags being used during the live firing depends on the distance to the target. Following a gun firing operation, discarded propelling charge increments were open burned near the gun position on the soil surface or on snow/ice in the winter (Figure 8 and Figure 9). Sampling conducted across Canadian ranges on the surface soils and in the underlying groundwater demonstrated that burning residues were deposited and represented a threat to the environment and human health.

A recent fate study conducted by INRS-ETE using large scale columns demonstrated that 500 g of burning residues spread over a 1 m<sup>2</sup> surface on the soil surface may lead to the contamination of more than 7.5 million liters of groundwater (GW) in the first infiltration [93]. Contrary to the particles deposited at the gun mouth which lead to a very slow dissolution rate of 2,4-DNT or NG, open burning lead to a highly leachable fraction of 2,4-DNT which is rapidly brought to the GW. This can be explained by the preferential combustion of the NC matrix, leaving highly leachable 2,4-DNT at the soil surface. This situation mandated the development of a safe and environmental alternative destruction method for the excess propelling charges.



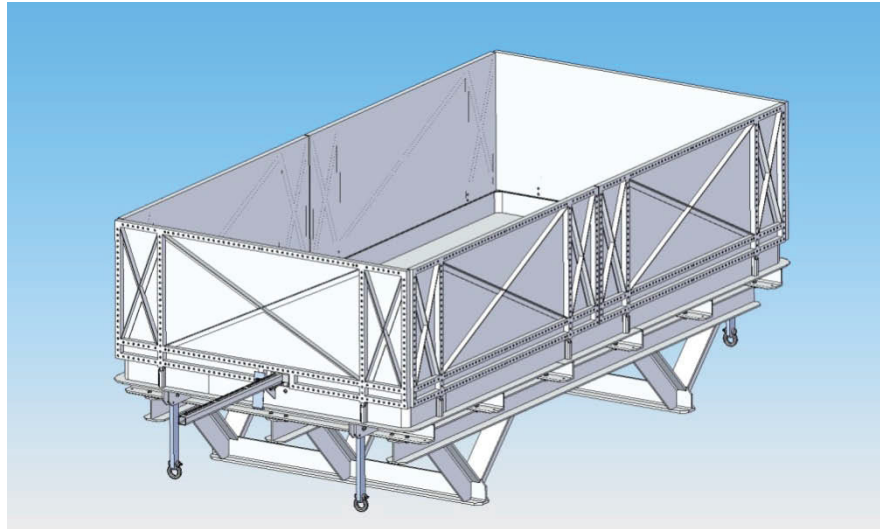
*Figure 8. Field expedient burning of excess artillery propellants.*



*Figure 9. Left over residues after burning on snow.*

A burning table to dispose the excess artillery propelling charge bags was developed to replace the field expedient burning of the excess charges on the surface soils or on snow/ice which greatly reduced the environmental footprint of artillery live fire training. The proven accumulation of 2,4-DNT and lead in the environment was stopped and the use of the table allows the safe destruction of excess propelling charge bags and sustainable artillery training. The table design was completed (Figure 10) and so far, 20 tables were deployed across Canada [94]. Therefore, only past burning activities shall be looked into in relation to the sampling plan design.





*Figure 10. Schematic of the Canadian excess artillery propellant burn table.*

Overall, the following areas shall be considered potentially contaminated by propellant residues in RTA's FP:

- In front of guns FP, from small arms to 155 mm calibers;
- Behind and in front of antitank rockets FP;
- At former excess propellant field expedient burning sites.

#### **2.1.2.2 Target impact area**

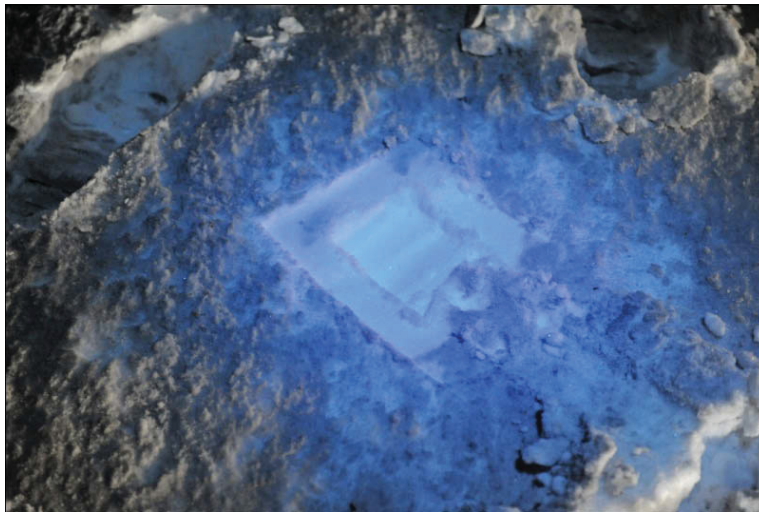
Target impacts areas were highly suspected of being contaminated by explosive residues. Many trials were dedicated to better understand the deposition pattern of explosive residues from various scenarios [40]- [48], [95], [96]. The conclusions drawn from this work are presented in this sub-section. The following sources of explosives have been studied: high-order detonations, low-order detonations, UXO blow in place, UXO shell cracking and UXO corrosion.

##### **2.1.2.2.1 High-order detonations**

High order detonations are defined as detonations that reach the desired pressure and detonation velocity. The evaluation of explosives deposition following high-order detonations is not a simple task. The detonation process involves high pressure and temperature and the deposition pattern can be very complex to assess. Various trials were conducted and led to the development of a set-up involving detonation on pristine snow cover which allowed an easier delineation of the deposition plume (Figure 11 and Figure 12). Table 5 presents representative high-order results obtained with mortars, hand grenade and artillery rounds.



*Figure 11. High-order detonation on snow profile.*



*Figure 12. Collection of residues from high-order detonation on snow.*

*Table 5. Mass of explosive deposited from high order detonations.*

<b>Weapons system</b>	<b>Explosive</b>	<b>Number of round fired</b>	<b>Percent of unburned explosive deposited</b>	<b>Mass deposited per round (µg)</b>
Mortar 60 mm	RDX	11	$3 \times 10^{-5}$	94
Mortar 81 mm	RDX	5	$2 \times 10^{-3}$	8500
Mortar 81 mm	TNT	5	$3 \times 10^{-4}$	1100
M67 Hand grenade	RDX	7	$2 \times 10^{-5}$	25
Howitzer 105 mm	RDX	9	$7 \times 10^{-6}$	95
Howitzer 105 mm	TNT	9	$2 \times 10^{-5}$	170
Howitzer 155 mm	RDX	7	$5 \times 10^{-6}$	310

As illustrated in Table 5, the quantities of explosive deposited are very small, almost at the forensic levels. The quantities are spread over large areas, and do not lead to the build-up of concentrations of concern of explosives. When sampling in various RTAs, many high-order detonation craters were sampled and showed no detectable trace of explosives.

#### **2.1.2.2.2 Low-order detonations**

Low-order detonations might happen in various scenarios in live firing events. A large percentage of the fired munitions function as designed and generates high-order detonations. A fraction varying from 1 to 50 % of rounds might generate low-order detonations or UXO. The failure rate of munitions depends on the type of round and in general, artillery rounds have a malfunctioning rate around 1-5 % while antitank rockets have proven to lead to a rate as high as 50 % in some occasions. A low-order detonation is defined as a detonation that does not reach the maximum detonation pressure and temperature and is sometimes referred to as a deflagration. The pristine snow set-up was used to monitor explosive residues from low-order detonations. They were achieved by using a weak detonation trigger [40]- [43].

It was found that while high-order detonations deposit µg of fine explosive dust, low order detonations deposit gram quantities of explosives from fine dust to large chunks. Figure 13 presents particles collected from a low order detonation of an 81 mm mortar shell. Table 6 presents deposition results measured from low-order detonations or mortar and artillery shells.



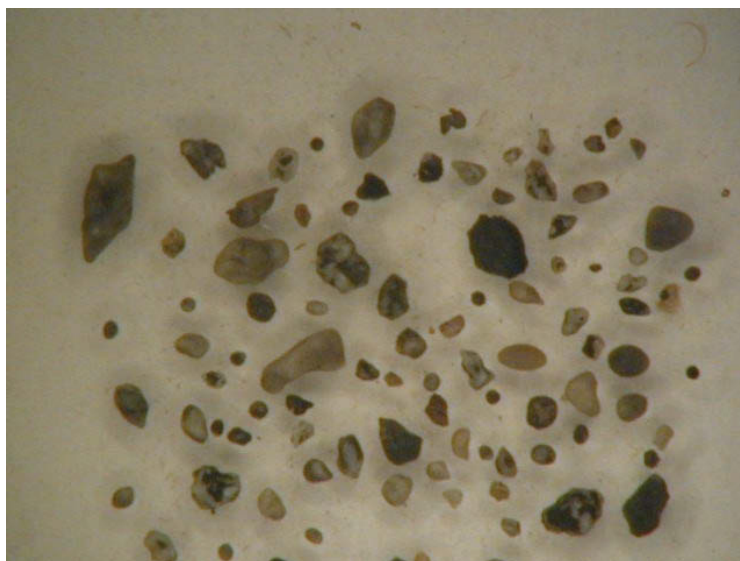


Figure 13. Comp B particles from low-order detonation of a 81-mm mortar.

*Table 6. Mass of explosive deposited from low order detonations.*

<b>Item</b>	<b>Explosive fill</b>	<b>Percent of unburned explosive deposited</b>	<b>Mass deposited (g)</b>
Mortar 60 mm	Composition B	35	67
Mortar 81 mm	Composition B	42	300
Howitzer 105 mm	Composition B	27	620
Howitzer 155 mm	TNT	29	2000

When sampling RTAs, low order detonation sites were encountered where the presence of high concentrations of explosives was always detected. Figure 14 and Figure 15 present low order detonation craters samples in Gagetown and Cold Lake RTAs. The reddish color of the pond indicated the presence of TNT photo-degradation by-products. This was confirmed in both cases.



*Figure 14. Low order detonation artillery crater in Gagetown RTA.*



*Figure 15. Low order detonation crater in Cold Lake RTA.*

#### 2.1.2.2.3 UXO blow-in-place (BIP)

In order to solve the safety risk that a surface UXO represent in our RTAs, Explosive Ordnances Disposal (EOD) team regularly proceed to UXO blow in place using C4 blocks to detonate the UXO without moving it.

The impacts of disposal operation conducted on RTAs when encountering UXO by detonating them with C4 is now better understood. The use of unconfined C4 blocks generates the dispersion of RDX in the surrounding of the detonation point [40]-[46], [95], [96]. Moreover, the probability of leading to low order detonations when doing BIP is higher than in a live firing context, as the UXO can be partially buried or in a configuration that does not allow high order event when initiating it with the C4. Finally, in a BIP event, the round does not function as designed (detonation from inside the casing) which may lead to lower order detonations. Another aspect of DRDC's research is dedicated to the improvement of the BIP procedure to minimize or else eliminate the dispersion of explosives when doing so. In the meantime, BIP using C4 is still conducted on a regular basis on Canadian RTAs. Therefore, locations where intense BIP has been conducted might present measurable concentrations of RDX from the C4 and also of other explosives from the UXOs. Demolition ranges where most of the BIP exercises are conducted therefore present in general higher concentrations of MC, namely RDX.

The major conclusions from the high- and low-order detonation and blow in place experiments are:

- A forensic (very small) amount of explosives is deposited when a round is functioning as designed.
- BIP detonations deposit a greater percentage of residues than live fire high-order and deposit RDX from the C4 donor charge.
- By far, the largest explosive residues deposition is from low-order detonations and particles deposited range from micrometers to centimetres in diameter.
- **As a rule of thumb: it takes 10,000 to 100,000 high order detonations to deposit the same amount of explosive than one low-order detonation.**

#### 2.1.2.2.4 UXO shell cracking

An important source of explosive in RTAs was identified through the quest for understanding the explosive contamination pattern in RTAs. Surface UXOs in impact areas are susceptible of being hit by razor sharp flying fragments from close proximity high order detonations. Designed experiments using 81 mm mortar shells demonstrated that this phenomenon is very easy to achieve and led to g to kg quantities of explosives in the surrounding environment [66]. This indicates that the surface to near surface UXOs which are exposed to other rounds that explode nearby represent an important source of explosive in the surface soils. The broken shells can release as much as the totality of their explosive content in the environment. Figure 16 and Figure 17 highlight the set up used to mimic the cracking of surface UXO by using a donor round nearby another round (UXO surrogate) and the resulting cracked round. Figure 18 illustrates cracked UXOs that were encountered in RTAs. During his Ph. D. thesis, Lewis *et al.* studied the risk to

the underlying groundwater caused by the presence of cracked UXOs [66]. This will not be discussed here, as another protocol will be written for groundwater survey and characterization.



*Figure 16. Set up to study the cracking of UXOs using a donor round.*



*Figure 17. Resulting cracked UXO.*





*Figure 18. Cracked rounds found in an RTA.*

This source of explosive residues stresses the need for regular clearance of surface UXOs in RTAs. EODs normally take care of the UXO by BIP as soon as they identify one. The regular elimination of surface UXO from highly used impacts areas such as artillery impact central area might not be always feasible and therefore, cracked UXOs shall be looked for when sampling for explosive residues in target impact areas and the surrounding area must be sampled. If feasible, remains of the cracked UXO shall be eliminated either by detonation or else by collecting the large chunks of explosives that may remain on site.

#### **2.1.2.2.5 UXO corrosion**

Corrosion of the munitions casings represents a long term source of explosives in the environment. The contamination risk would be higher for the underlying GW as most of the UXOs are buried in the soil profile at various depths, which can go down to few meters for air-

soil large calibers rounds. The corrosion rate is a complex phenomenon which depends on soil conditions, on heating/cooling and wet/dry cycles, on soil physico-chemical characteristics and many other parameters. Consequently, DRDC is studying munitions corrosion rates at CFB Petawawa in a long term study as part of its environmental impacts analysis (Figure 19). For the sake of this report, it will be assumed that corrosion represents a long term source term, that is still undefined and that most of the risk is not related to surface soils but to GW. Corroded surface UXO shall still be identified and reported to range control for further BIP if ever encountered in RTAs.



*Figure 19. Corrosion study ongoing at CFB Petawawa.*

## **2.2 Metals**

The precise knowledge of the metallic composition of munitions is generally unknown, because this kind of information is generally proprietary of the manufacturer. Nevertheless, the following sub-section provides an overview of the main known sources of metals in RTAs as well as their deposition processes.

### **2.2.1 Sources of metals in RTAs**

Metals are deposited onto range soils by a variety of processes. High-order detonations generally disperse very fine metal particles in RTAs, with the exception of pre-fragmented rounds which might produce large fragments even in high order scenarios. Much larger fragments are generally produced by low-order detonations.

As opposed to energetics, which are mostly transformed into combustion gases (e.g., carbon monoxide, carbon dioxide, water, methane, ammoniac, etc. during the detonation, metals are not destroyed by the detonation. However, they can be transformed in other metallic compounds not originally present in the munitions. This transformation can occur either during the detonation process or to weathering of the metallic particles deposited on the range. Both processes are extremely different and generally lead to the formation of different metallic compounds. For example, during a detonation event, the temperatures and pressures reach extremely high values that exceed the melting temperatures of some of the metallic compounds present in the munitions. These molten species are then free to react with other compounds to form new alloys, metallic complexes or salts, which will all have their own environmental fate.

Weathering consists in breaking down the metallic particles or fragments through contact with the atmosphere, biota and water. Two important classifications of weathering processes exist – physical and chemical weathering. Physical weathering involves the mechanical breakdown of metallic particles or fragments through direct contact with atmospheric conditions, such as heat, water, ice and pressure. Physical weathering causes the disintegrations of metallic particles or fragments, often via abrasion, without chemical change.

Chemical weathering rather involves the direct effect of atmospheric chemicals or biologically produced chemicals in the breakdown of metallic particles or fragments. Chemical weathering is a gradual and ongoing process as the mineralogy of the metallic particles or fragments adjusts to the near surface environment. Chemical weathering changes the composition of metallic particles and fragments, often due to contact with water. Oxidation, hydrolysis and carbonation are the most common transformation reactions observed.

Chemical and physical weathering are simultaneous processes. The physical weathering may induce cracks in fragments, which will then be exposed to chemical weathering. Alternatively, the chemical action in cracks can help the disintegration process. The materials left over after the metal particles break down combine with organic material to create soils.

To summarize, the metallic composition of most munitions is unknown, preventing calculations of source terms. In addition, upon detonation or weathering, metallic particles and fragments can transform into different metallic compounds that all have their own environmental fate. Therefore, all the metals originally present in munitions are dispersed in RTAs after detonation, either in their original state, or as other metallic compounds. An overview of the most important factors affecting the environmental fate of metallic residues dispersed in the environment is provided in sub-section 2.3.2.

#### **2.2.1.1 Firing positions**

Metals at firing positions generally comes from the detonation of the primer, from the combustion of the gun propellant, from the erosion of munitions or weapon during the firing event [60], or from large metallic parts ejected from the weapon during the firing, such as small arms cartridge cases. The metals that could be expected would mostly be copper, zinc, lead and mercury. Firing positions are generally small areas on which contaminants could potentially accumulate very fast. However, metallic species are seldom detected at firing positions in concentrations above guidelines, mainly because of the small quantities of metals contained in primers and propellant,

and of the small quantities eroded during the firing event. Large metallic parts, such as casings, are recovered by the users after the training activity.

#### **2.2.1.2 Target area**

In general, medium and large caliber munition projectiles are made of steel (an alloy of iron (Fe) and carbon) or aluminum (Al). Small caliber bullets mainly contain lead (Pb), antimony (Sb), arsenic (As), copper (Cu) and zinc (Zn), and grenade bodies are generally made of brass, a Cu-Zn alloy. Fe and Al are ubiquitous in the environment and of little concern, but Pb, Sb, Cu and Zn are regulated by CCME. In addition, a wide variety of metals is also present in the other parts of the munitions (e.g., fuze, booster and primer cups, cartridge, tail, stabilizing fins, primer tube, connecting elements, percussion pin, etc), albeit in smaller quantities. For example, the 60-mm mortar contains Fe in the shell, aluminum, Zn, magnesium (Mg) and Cu in the tail and the stabilizing fins, and Al, Cu, bismuth (Bi) and Pb in the cartridge. Primary explosives also constitute another source, albeit small, of heavy metals such as Pb or mercury (Hg). The list of contaminants targeted for analysis in small arms range is shown in Table 7.

Most of the metallic debris deposited in the impact areas of RTAs come from the munition casings and are located in the vicinity of targets. However, an important source of metals in RTAs that is often overlooked is the targets themselves (e.g., old tanks, cars, trucks, etc.) that can be partly disintegrated by the detonation of munitions into metallic debris of various particle size and compositions. These metallic debris also have an environmental impact and should not be neglected when performing an environmental risk assessment.



Table 7. Constituents of small arms munitions (reproduced from [134])

Constituent	Symbol	Source
Lead	Pb	Primary constituent of most projectiles
Lead styphnate/ lead azide		Primary constituent of most primers
Antimony	Sb	Hardening agent
Antimony Sulfide		From 5% to 30% is used in most primer compounds
Arsenic	As	Lead shot constituent (used in the production of small shot since it increases the surface tension of dropped lead, thereby improving lead shot roundness)
Copper	Cu	<ul style="list-style-type: none"> <li>• Sometimes a primary alloy in center-fire ammunition and some small caliber rifle bullets;</li> <li>• also used in frangible pistol ammunition</li> <li>• Jacket alloy metal (Increases hardness)</li> </ul>
Bismuth	Bi	Lead shot replacement
Tin	Sn	Primary metal for center-fire ammunition and shot (Increases hardness)
Zinc	Zn	Jacket alloy metal
Iron	Fe	Iron tips on penetrator rounds and steel shot (has been used successfully to remediate high levels of lead and arsenic in some soils)
Tungsten	W	Alternative projectile material to lead (Recent research indicates there may be some adverse environmental and human health concerns regarding tungsten)
Nickel	Ni	Coating to improve shot performance
Cobalt and Chromium	Co and Cr	Alloys in some ammunition rounds

## 2.3 Fate and transport

The behaviour of contaminants exposed to environmental conditions should be considered when characterizing a contaminated site. This section will briefly present the general mechanisms that govern the fate and transport of MC.

### 2.3.1 Energetic materials : explosives and propellant

In general, explosives and propellants have low vapour pressure (see Table 1). Therefore, their fate is driven by dissolution/leaching, transformation and mineralization. NG and 2,4-DNT have higher vapour pressure but when dispersed in a NC matrix, volatilization is highly limited.

The fate and the risk associated with a contaminant are closely related, as illustrated in the conceptual model presented in Figure 20. The risk is associated to the effect of each MC, their metabolites and their fate. Their fate is driven through transport and degradation.

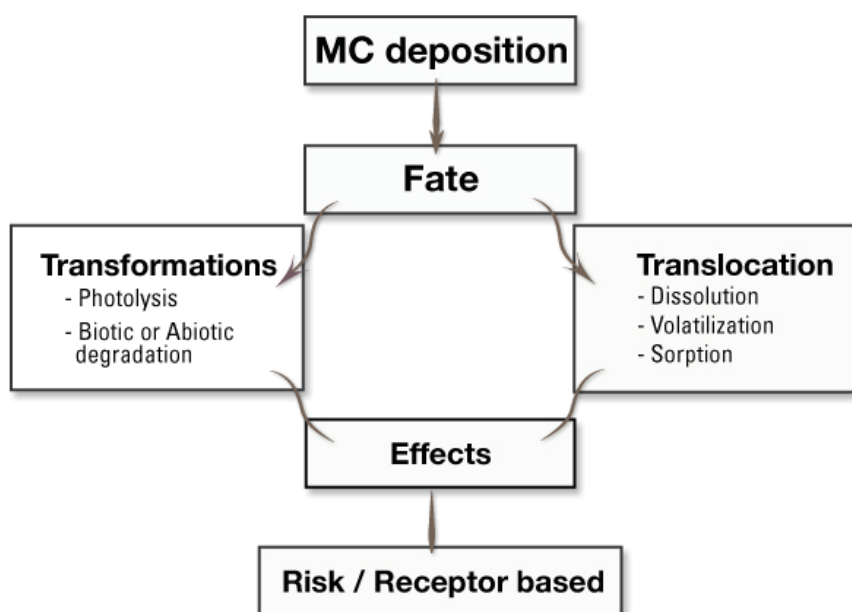


Figure 20. Conceptual model for the environmental fate of MC.

The nature of the particles that are dispersed in the environment is critical, as it strongly influences the fate of contaminants. As presented earlier, explosives are dispersed as crystalline solid particles of heterogeneous nature while propellants are deposited as fibrous materials of either 2,4-DNT or NG embedded in a NC matrix. Propellant residues have a long term environmental residence since they are embedded in a NC matrix that protects them from dissolution and further biotic or abiotic processes [62] [92]. Therefore, the risk to the GW is low and most of the MC remains at the soil surface in the first 2.5 cm of soil for many years, even decades. One exception is 2,4-DNT liberated by field expedient burning of excess artillery propellants. As stated earlier, even though this activity is now banned in Canada, it still can be

conducted under rare circumstances. In these cases, there is a fraction of highly leachable 2,4-DNT that is available to dissolution and degradation processes. The remaining fraction is embedded in NC and will remain at the soil surface for years.

Composite rocket propellants may lead to the dispersion of ammonium perchlorate (AP) in the environment. When fired from air-to-soil, a detonation of the rocket prior to complete burning of the propelling charge or else a malfunctioning of the rocket and breaking of the casing upon impact may lead to the accumulation of AP in the surface soils. It has been demonstrated [52] that when normal functioning occurs, the combustion in the rocket is very effective and AP is not dispersed in RTA. AP is also included in a few other weapons such as M72 antitank rocket propellants or smoke formulations. AP is highly soluble and does neither binds to soil matter nor transforms readily in the environment so it will rapidly be brought to the groundwater table and can travel out of the RTA boundaries. It is therefore a critical parameter to monitor in surface and groundwater as soon as one type of AP-based munitions is used in a specific range. Quantifying AP in surface soils has never been done, as it is so soluble that after only one rain event, it would not be detected in the surface soils.

The explosives mostly used in Canadian ammunitions are TNT-, RDX- and HMX-based and a lot of efforts were dedicated to better understand the complex fate and transports mechanisms of propellants and explosives [67][68][69][70][73][74][75][87]. A good overview of the main process descriptors for explosives has been published by Brannon *et al.* [98].

The environmental fate of explosives can be attributed mostly to their molecular structure and related water solubility, their adsorption to soil particles and the production of metabolites through biotic and abiotic routes. In other terms, the main processes that control their fate are: solubility and dissolution, adsorption, transformation, biodegradation, photolysis and volatilization. For instance, TNT is a nitroaromatic and tends to degrade by photolysis, while nitramines like RDX and HMX can be photodegraded but to a much lower extent. Some photodegradation of TNT by-products are well known, while other species are still to be determined. TNT is also more soluble and dissolves more rapidly in water than RDX or HMX (HMX being the least soluble). TNT can degrade into more than 20 different metabolites with various solubilities and toxicities [74]. For example, the aminodinitrotoluenes (ADNTs) that result from the photolysis or biodegradation of TNT are much more soluble than the parent compound, but they can easily covalently bind to humic acid. Therefore, these metabolites are stabilized by the formation of an amide with the organic content of the soil. Moreover, in soils that contain clays, sorption mechanisms are stronger with TNT and its metabolites than for RDX and HMX, which adsorb very poorly to clay mineral [99].

Therefore the relative rates of soil leaching of these three explosives can be explained in terms of the relative water solubilities and adsorption strengths. RDX leaches out faster than TNT, which in turn leaches out faster than HMX. TNT and its metabolites are more soluble than RDX, but their migration is inhibited by strong bonding interactions with soil constituents. On the other hand, HMX has a tendency to remain at the surface of the soil, because it is almost insoluble in water. Interactions with the soil are an important factor when characterizing explosives in terms of bioavailability and extractability. TNT is particularly difficult to characterize because it is easily reduced to amino degradation products, namely 2- and 4-amino-dinitrotoluene (2- and 4-ADNT), 2,4- and 2,6-diamino-nitrotoluene (DANT), and, under anaerobic conditions, 2,4,6-triaminotoluene (2,4,6-TAT). The characterization of TNT derivatives is important in establishing

its overall toxicity, transport, and extractability or bioavailability. The adsorption and desorption characteristics of TNT and its metabolites are important physical factors to consider when assessing the availability of the compounds to microbial degradation and physical analysis. Additional R&D effort is needed toward the development of an optimal extraction method for TNT metabolites that are strongly bound to clay or organic soils. All data acquired up to now tend to indicate that most TNT metabolites are rapidly strongly sorbed to soil humic acid, if not irreversibly, which limits greatly their bioavailability. Therefore, even if TNT and its metabolites are considered toxic, they are not readily available for receptors. All MC can be partially bioaccumulated in the biomass and plant uptake and this has been studied as a remediation mean.

In conclusion, MC are mostly found in the top surface soils and vegetation in RTAs from 0 to 2.5 cm deep. Surface soils including the vegetal covers whenever present must be analyzed for energetic materials included in EPA 8330b method, as well as surface and groundwater. RDX and HMX are the most probable explosives that might be detected both in the surface soils and in surface and groundwater as they are not easily solubilised and then weakly retarded or bound by the soil matrix. NG and 2,4-DNT are the two most probable propellant constituents in FP surface soils. TNT is more soluble than nitramines but has rarely been detected into both RTA surface soils and GW, as it rapidly transforms and binds to the soil profile. One exception to this are TNT-filled munitions low order sites where TNT was detected both in the soil and surface water.

### **2.3.2 Metals**

The fate and transport of heavy metals in the environment will depend strongly on their solubility in water and their bioavailability, i.e. their capacity to bind to the soil constituents. A metal compound with a high solubility and a low binding capacity has a higher mobility and presents a larger potential for leaching in groundwater and/or travel far away from the range. However, a compound having a low solubility will most probably stay on the surface of the soil, and a compound with strong binding affinities will most probably stay either on the surface or in the subsurface, where a specific bonding agent is encountered. In addition, small particles tend to be more mobile, either in solution or as colloids.

The water solubility of heavy metals in their elemental state is generally low. However, heavy metals do not generally remain in their elemental form when they are exposed to weathering and water. They are easily oxidized in their ionic form and will form various salts with soil constituents, all having a different solubility and bioavailability. As a general rule, nitrates, chlorides, bromides and acetates are readily soluble in water, and sulphides are considered to be insoluble. However, the solubility of hydroxides, sulphates, phosphates, and carbonates will vary depending on the heavy metal counterpart, and on the pH of the water. The lowest solubilities are generally observed in neutral pH water (6.5 to 7.5). Acidic water ( $\text{pH} < 6.5$ ) tends to increase the solubility of most metals salts, while basic water ( $\text{pH} > 7.5$ ) will either induce the precipitation and immobilisation of an insoluble heavy metal compound, or increase its solubility, depending on the heavy metal. Thus, extreme caution must be exercised when trying to decrease the leaching of soils containing multiple heavy metals by controlling the pH of the soil, because the solubility of some heavy metal compounds may increase when exposed to basic pH.

Key parameters governing the bioavailability of a given heavy metal compound are the composition (organic matter, metallic constituents) and pH of the soil, the particle size distribution, and the contact time between water and the heavy metal compound. These

parameters govern in turn measurable, macroscopic parameters, such as the type of soil (sand, silt, clay, etc), the cation exchange capacity (CEC), and the reduction-oxidation (redox). The binding capacity tends to increase with the decrease of soil particles size. For example, absorption in clay is much higher than in sand, because the groundwater movement in clay is slower, and also because the surface area of soil particles to which heavy metal component can bind is higher. In consequence, sandy soils present the highest leaching potential. The contact time between water and the heavy metal compounds is controlled by the amount of annual precipitation and the rainfall intensity. The absorption of several heavy metal compounds to soil components also tends to increase with the cation exchange capacity. And the redox potential will affect the type of heavy metal compound that is stable in a given area. The bioavailability of heavy metals and factors affecting it is a very complex subject, and a thorough review is beyond the scope of this document. Interested readers may consult appropriate references, such as the CCME Canadian Soil Quality Guidelines[4], for more information.

The mobility of heavy metals is also affected by external physical factors, such as the topographic slope and the intensity of wind. Particles of heavy metal compounds or dissolved heavy metals can indeed be moved by storm water runoff. The ability of water to transport lead is influenced by two factors: velocity of the water and weight or size of the lead fragment. Water's capacity to carry small particles is proportional to the square of the water's velocity. Clear water moving at a velocity of 100 feet per minute can carry a lead particle 10,000 times heavier than water moving at a velocity of 10 feet per minute. Muddy water can carry even larger particles. A shallow groundwater table is indicative of potentially higher risk for mobilized heavy metals to reach the groundwater. The shorter the distance the contaminant has to travel to the GW or the SW, the greater is the risk of migration of heavy metals towards receptors.

## **2.4 MC environmental and health related thresholds**

### **2.4.1 Explosives and propellants**

MC are relatively recent contaminants of concern. Until recently, there were neither soil quality guidelines nor threshold published for these compounds. This section will present very briefly the human health risk information related with main MC and the published environmental and health related guidelines in Canada and the U.S. In general, there are no accepted Canadian guidelines for MC in surface soils, while the U.S. EPA drinking water guidelines are applied in Canada for water samples.

TNT is considered a possible human carcinogen based on evidence from animal experiments. Rats exposed to TNT in long-term ingestion studies developed bladder cancer and other health problems such as anaemia, abnormal liver function, skin irritation and cataracts [100]. Technical grade DNT is constituted of approximately 78% 2,4-DNT and 19% 2,6-DNT, and small amounts of other isomers. DNTs are absorbed through the gastrointestinal and respiratory tracts and by skin absorption in most species. 2,4-DNT and 2,6-DNT have been classified as possible human carcinogens by the International Agency for Research on Cancer (IARC) [101]. Both RDX and HMX can cause nervous system problems if ingested in large quantities [102], [103]. NG is a well know vasodilator, may cause drop in blood pressure, headache, dizziness, nausea, vomiting and palpitations [104]. Ammonium perchlorate may present a risk of thyroid malfunction and may cause in the long term decreased mental performances and altered child development [105].

The reader interested to the ecotoxicological impacts of main MC can consult Sunahara's book, published in 2009 [80].

In Canada, the National Research Council developed ecological and human health based guidelines for use at active RTAs to protect the environment and insure sustainability, or Soils Concentrations for Ensuring Military Training Sustainability (SCMTSE) [81]. These guidelines are the first known set of MC guidelines published worldwide. They have recently been updated, under the request of DGE, and these 2011 updated guidelines are presented in Table 8. They can be used as flag values, where concentrations of concern are detected. Whenever concentrations are detected over these flags values, actions might be taken such as regular sampling at the same location, installation of groundwater wells down-gradient, remediation, modification of the activity to minimize the accumulation of MC and removal of the source when possible.

*Table 8. Military soil quality guidelines for EM*

<b>Compound</b>	<b>SCMTSE (mg/kg)</b>
TNT	9.6
RDX	7.7
HMX	89
2,4-DNT	6.7
2,6-DNT	10.6
NG	54

Concentrations of MC can be compared to environmental quality guidelines in order to assess risk to human health and the environment. Various provincial and federal guidelines are presented below. Since guidelines are periodically updated, the guidelines presented in this subsection are for information purposes only, and the source documents should be consulted to obtain the most up to date information.

In Canada, the environmental regulatory agencies in British Columbia (BC), Ontario and Quebec developed environmental guidelines for selected EMs. In the United States, U.S. EPA Regions 3, 6 and 9 have also developed guidelines for selected EMs. The U.S. EPA, BC, Ontario and Quebec guidelines are presented in Table 9 to Table 12.

The U.S. EPA Region 3 and 9 developed guidelines for EM in 2004 and revised these guidelines in 2008 to take advantage of new scientific information and to harmonize the guidelines across Regions 3, 6 and 9. The 2008 guidelines are presented in Table 9. These risk-based guidelines (screening levels) were developed from standardized equations combining exposure information with U.S. EPA toxicity data. The guidelines are based on human health and do not include ecological receptors. They were derived from direct human contact exposure values that include soil ingestion, particulate inhalation and dermal contact, but do not include the ingestion of food

grown on contaminated soils. For EMs that are considered carcinogenic, an increase of cancer risk of 1 in  $1 \times 10^6$  was used to develop the guidelines.

*Table 9. Environmental quality guidelines for EM in U.S. EPA regions 3, 6 and 9.*

Substance	Soil (mg/kg)	
	Residential	Industrial
2-Am-DNT	150	1,900
4-Am-DNT	150	2,000
1,3-DNB	6.1	62
2,4-DNT	120	1,200
2,6-DNT	61	620
RDX	5.5	24
NB	31	280
NG	6.1	62
2-NT	2.9	13
3-NT	1,200	12,000
4-NT	30	110
HMX	3,800	49,000
Tetryl	240	2,500
1,3,5-TNB	2,200	27,000
TNT	19	79

In 2009, the British Columbia Ministry of Environment developed guidelines for EM in a similar manner as the U.S. EPA. However, an increase in cancer risk of 1 in  $1 \times 10^5$  was used resulting in cancer based guidelines for RDX, NG, 4-NT and TNT being a factor of 10 higher than the U.S. EPA guidelines. The BC guidelines are presented in Table 10.

*Table 10. Environmental quality guidelines for EM in British Columbia.*

Substance	Soil (mg/kg)	
	Agricultural, urban park and residential	Commercial and industrial
ADNT (all isomers)	12	120
RDX	44	160
HMX	3100	31000
1,3-DNB	6.1	62
2,4-DNT	120	1200
2,6-DNT	61	620
NB	20	100
NG	350	1200
2-NT	8.8	22
3-NT	730	1,000
4-NT	120	300
Perchlorate	7.8	100
1,3,5-TNB	1,800	18,000
Tetryl	610	6,200
TNT	160	570

The U.S. EPA and BC guidelines are the most complete set of guidelines for EM and their transformation products in North America. The environmental regulatory agencies in Ontario and Quebec have also developed guidelines for a few EM.

In 1996, the Ontario Ministry of the Environment developed guidelines for the protection of human health and the environment for drinking and not-drinking groundwater situations (Table 11). The guidelines were established only for 2,4-DNT from the lowest value resulting from dermal contact, soil ingestion, groundwater contamination and vapour inhalation effects assessments for different land uses.



*Table 11. Environmental quality guidelines for 2,4-DNT in Ontario.*

Substance	Soil (mg/kg)		
	Agricultural and other	Residential, parkland and institutional	Industrial, commercial and community
2,4-DNT	0.66	0.66	0.66

The Quebec Ministry of Development of the Environment and of Parks has also developed guidelines for DNTs and TNT in soil and groundwater. The guidelines consider soil ingestion, dust inhalation, dermal absorption from dust and ingestion of produce grown on a residential site. Exposure through groundwater was omitted. The soil guidelines in Quebec are presented in Table 12.

*Table 12. Environmental quality guidelines for EM in Quebec.*

Substance	Soil (mg/kg)	
	Residential, recreational and institutional	Commercial and industrial
2,6-DNT	0.0002	0.03
TNT	0.04	1.7

In conclusion, in Canada, there are no federal environmental quality guidelines for EM. BRI has published military based guidelines applicable to RTAs. U.S. EPA and B.C. environmental guidelines are the most complete and available guidelines up to now.

## 2.4.2 Metals

A detailed exposure of the potential effects of heavy metals on the environment and on the human health is beyond the scope of this document. Interested readers are invited to consult specialized documentation [106][107]. Because most heavy metals are already regulated by the CCME [4] and several provinces, no specific military criteria were developed. The RTAs metal concentrations are generally compared to those of CCME Industrial Soil Quality Guidelines (ISQG) for the Protection of Environmental and Human Health (SQGPEHH) or to those of the appropriate provincial regulations. In case of range closure, the chosen criteria must be related to the future activities of the site (industry, recreation or agriculture).

### 3 Characterization approach

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Chapter 3 presents the general strategy to overcome heterogeneity, safety aspects when sampling surface soils in UXO contaminated ranges, soil sampling approach, related tools, sample processing and storage, relevant QA/QC and requirements that external laboratories must comply with. Good sample processing is as important as the sampling steps for MC due to the heterogeneous dispersion in the soil matrix. The list of equipment needed for sample collection is provided in Annex A.

#### 3.1 General sampling strategy to control heterogeneity

The general sampling guidances for soils that can be found in guidance documents such as CCME guidance documents from Quebec and Ontario should be integrated in the sampling strategy [108], [109]. In addition to that, specific guidances are needed to characterize RTAs, due to the nature of the dispersion of MC.

The nature of explosive and propellant dispersion comprises both compositional and distributional heterogeneity. The compositional heterogeneity is due to the intrinsic nature of the explosives and propellants: the formulations are complex and are inhomogeneous in nature from their conceptions. In other words, compositional heterogeneity is described as the variability of contaminant concentrations between the particles that makes the population which leads to a fundamental error (FE). As an example, melt-cast explosives such as Composition B are prepared by melting TNT, adding nitramines and cooling down the formulation in the shells. Depending of the cooling rate, sedimentation occurs to a certain extent, and the composition of the cold melt cast may differ between the bottom and the top of the round. Moreover, after detonation of the explosive or combustion of the propellants, the expelled grains may vary in their relative percentage of the various ingredients, as preferential combustion of component may occur. Finally, after exposition to the environment, some components in the grains can be dissolved at a faster rate than other, leading to particles that do not present the expected proportions of ingredients.

FE is managed by collecting and analyzing sufficient sample mass to address the compositional heterogeneity. FE is related to the particle size of the population and sample mass by the following equation:

$$FE = \sqrt{\frac{20 (d^3)}{m}}$$

Where

FE = Fundamental error

20 = Sampling constant

d = maximum particle size (centimeters)

m = sample mass

The importance of sample mass in reducing the FE is illustrated in this equation.

As shown previously in the particle deposition study, there is also a very high distributional heterogeneity in the dispersion of MC. Taylor *et al.* have studied extensively the high heterogeneous pattern associated with explosive and propellant distribution as illustrated in reference [110]. Solid particles may vary from very fine dust to large chunks of explosives, up to cm size and the pattern of dispersion in the soil surface is never the same. Spatial variability will be missed if all samples are collected in one place. This heterogeneity results in segregation error (SE).

**In order to minimize FE and compensate for compositional heterogeneity a greater sample mass must be collected and in order to minimize SE and compensate for the distributional heterogeneity multiple sub-samples must be collected.**

Due to the high degree of variability encountered both from a compositional and distributional perspective and also based on soil heterogeneities, soil sampling must be conducted by combining a number of samples from the depth of interest into one sample that is representative of both the identifiable sampling site and the depth increment. More specifically, it is recommended to use a composite sampling strategy with a judgemental systematic random sampling design to obtain a sample or replicate samples to characterize the average concentration of MCs within a chosen area or decision unit (DU). In general, a minimum of 30 to 50 random increments are needed. However, depending on the size of the DU selected, more increments can be needed. DUs will be further defined in the following subsections.

The entire sample should then be thoroughly homogenized to minimize sub-sampling variability. This approach is dramatically different from the collection of discrete samples and the commonly used practice of field splitting or laboratory sub-sampling by removing only a portion of the sample received from the field for further processing. Composite sampling is not a new concept and has been well documented [111]-[113]. The theory behind multi-increment soil sampling (MISS) was developed by Pierre Gy in the early 90's [114].

While composite sampling was not new, there was a very high resistance in the U.S. from the U.S. EPA to accept the application of compositing in RTAs characterization. They claimed that this leads to sample dilution and that discrete sampling was better appropriate. It took many case examples and sampling campaigns to prove the advantages of using what will be referred to as multi-increment soil sampling. Since then, a few States have accepted the application of MISS and draft guidances have been published both in Alaska and Hawaii [115], [116]. Dr Jenkins, Mr. Hewitt and Mr. Ramsey in the U.S. have been instrumental in convincing the U.S. EPA authorities that MISS must be applied in RTAs to obtain defensible and representative results [117], [118]. Mr. Ramsey refers to Multi Increment Sampling or MIS<sup>®</sup>, and has registered the acronym as a trademark of EnviroStat, Inc.

MISS is done by collecting a minimum of 50 small increments of soil from a specified DU and combining these into a single sample, referred to as the MISS. However, the larger is the number of increments, the better will be the sample representativeness. No general rules can be applied as sampling objectives must always be integrated in the sampling strategy, but Table 13 presents

a general guidance as to the minimum number of increments to use, depending of the size of the DU. A minimum of 50 sub-samples is recommended to form a MISS that weights between 1 and 2 kg.

*Table 13. Minimum number of increments recommended in function of the size of the DU.*

Size of the DU	Number of increments
0-10 m <sup>2</sup>	50
10-50 m <sup>2</sup>	75
50-100 m <sup>2</sup>	100

The size and location of the decisions units (DUs) is planned using the knowledge sufficient to delineate areas that are likely to be contaminated, or likely to have differences in background concentrations or in variability. It must also be closely linked to the sampling objectives identified in the early process. If done properly, it will separate out areas of high and low concentrations and/or variability, and reduce greatly the number of samples required to be analyzed. Based on the knowledge gained in RTAs past characterization, areas of the greatest interest for each type of firing ranges will be defined. Judgemental sampling is then appropriate to select the sampling locations i.e., they are chosen solely on judgement, one location at a time. The biases of the sampler becomes dominant in choosing locations, but this method is useful when the sampler has excellent knowledge of the site and where it is thought to be significant contamination present from a number of sources.

Systematic planning and clear articulation of project objectives are the essential foundations for designing any sampling plan. Determining the primary end use of the data is of primary importance. The sampling design will help in the definition of DUs. DU can be defined as an area where a decision is to be made regarding the extent and magnitude of contamination with respect to the potential environmental or human health hazards posed by the existing or anticipated future exposure to contaminants.

The following parameters must be taken into account when planning the DUs size and location:

- 1- Contaminant expected;
- 2- Field observations (munitions debris, craters, low order evidences, cracked UXO evidences, burn residues, explosive and propellants particle evidences);
- 3- Past and future land use;
  - a. What was the past use: Was it a FP? A target impact area? A demolition range?
  - b. Has the surface been altered or material removed?

c. Will this site be closed and used for any other land use?

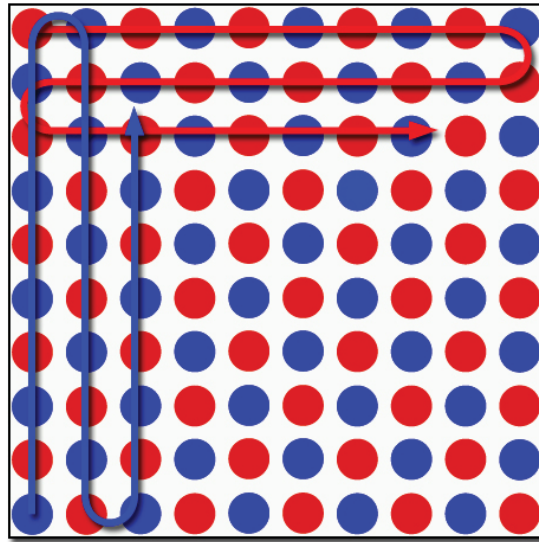
4- Receptor exposure scenarios.

The primary objectives in RTAs characterization are:

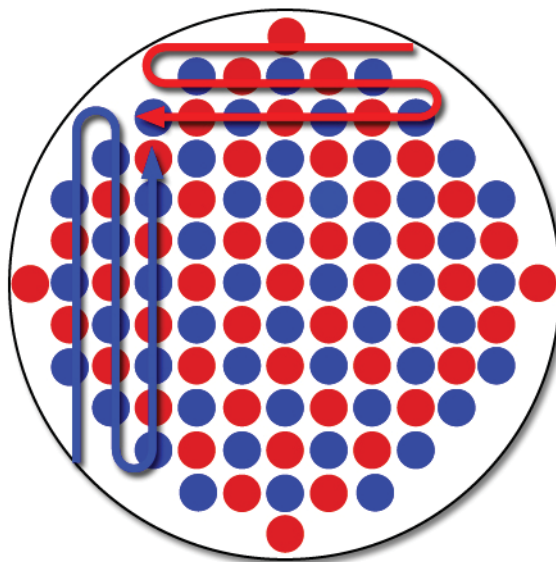
- 1- To measure the surface soil contaminants that may pose a threat to the health of military users that may come in contact with the contaminants (human exposure);
- 2- To measure the surface soil contaminants that may further be dissolved and brought to the surface water bodies and trigger the Canadian Fisheries Act;
- 3- To measure the surface soil contaminants that may further be dissolved and reach the GW and further reach the boundaries of the RTA properties and reach sensitive receptor through drinking water wells, crop irrigation or resurgence;
- 4- To measure the surface soil concentrations that may pose a threat to local ecological receptors (ecotoxicity);
- 5- Combination of some or all the above.

DU size and location may evolve with time if multiple sampling campaigns are conducted. In RTAs, DUs are smaller portions of the range that are based on the munitions used and the expected MC deposition pattern. Wide area assessment can be firstly conducted to assess the concentrations over large areas, and smaller DU can then be achieved to better delineate the pattern of contaminant dispersion. RTAs are generally characterized in two to four phases in the spring to fall seasons, and DUs locations and size are further defined as the process takes place. When GW sampling is conducted in parallel, GW data can lead to a more precise location of the DUs, whenever contaminant tracking back is needed. In other words, when MC are detected in GW, sampling DUs in the soil surface up-gradient of the GW flow is needed to determine the source of GW contamination. When considering the vast acreage covered by some live firing ranges, such as artillery ranges, even large DUs can be seen as almost discrete samples (e.g. DUs of 100 m<sup>2</sup> to represent 4 km<sup>2</sup>). An individual DU should encompass an area having similar characteristics throughout.

As stated earlier, the recommended approach for sampling DUs is a **judgmental systematic random approach**. The **judgmental** term refers to the fact that the sampling team judgment is the key to DU positioning and size. The DU is walked in a serpentine matter and increments are collected at each 3 to 4 steps, in the same area of the sub-unit. When all the surface of the DU is covered, the same process is repeated after a rotation of the sampling path by 90°, as illustrated in Figure 21 and Figure 22. The **systematic** term is related to the perpendicular systematic paths, while the **random** term refers to the fact that any corner of the DU can be selected to begin the sampling process. Some DU may be of irregular form, and in that case continuous Global Positioning System (GPS) monitoring is needed. In the case where circular DUs are selected, the GPS location of the center of the circle is needed, while in square or rectangular DUs, the four corners GPS locations must be recorded.



*Figure 21. Sampling pattern for optimizing sample representativeness in a square or rectangular pattern.*



*Figure 22. Sampling pattern for optimizing sample representativeness in a circular pattern.*

DUs can be of any shape that will best meet sampling objectives – rectangular, circular, concentric rings, radial wedges from a release point, irregular shapes. In some instances, decision units circumscribing a feature (tank or target or building) may be appropriate. Where practical, rectangular shape DU is recommended for ease of sampling. 100 to 200 m<sup>2</sup> DU and larger have successfully been used to map explosive residues on active ranges. For larger DU, the sample mass needs to be larger than 2 kg such as up to 5-7 kg.

Using MISS, reliable estimates of mean concentrations for the specified area of virtually any size can be obtained. Reproducibility between properly collected replicate samples shall be lower than 30 % relative standard deviation (RDS). Data distribution of replicates samples tends to be of a normal distribution as opposed to skewed for discrete samples. Normally distributed data simplify statistical evaluations and precision can be quantified using relatively few samples or replicates. Levels of statistical confidence and decision uncertainty that would require a very large number of discrete samples are obtained using only a few MISS. Thus, results will not be sampler-dependant and anybody who follows the sampling scheme shall end up with replicate samples with < 30% RDS.

In conclusion, MISS must be applied in DU following these rules:

- 1- Subdivide the DU into a uniform grid cells, e.g. 100 cells if you want 100 increments;
- 2- Mark the limits of the DUs and put as much marker flags to insure the systematic sampling of the DUs;
- 3- Randomly select a single increment collection point in the initial grid cell;
- 4- Collect increments from the same relative location within each of the other grid cells by walking the DU in a serpentine manner until complete covering of the DU.
- 5- Whenever the sampling location is not appropriate (e.g. large rocks) move as little as possible away to collect the increment;
- 6- Try not to be influenced by the visual observations (sampling only where you see contaminants)
- 7- Redo step 3 using a perpendicular grid;
- 8- When doing a field duplicate, randomly select a different starting point than in step 2 and repeat steps 3 and 4.

This process is straightforward in a square, rectangular or circular DU but it can be challenging in irregular DUs. The sampling must then be conducted to lead to the most systematic approach as possible.

The number of lanes within the decision unit and the increment spacing to collect the proper number of increments and the desired sample mass has to be assessed. A first attempt is conducted and if the desired outputs are not obtained, the lanes and spacing is adjusted and the sampling is redone.



### **3.1.1 DU for risk-based human health soil screening levels**

The risk-based screening involves that the DU must be representative of the human health exposure unit. The assumption is in that case that human receptors exposure is the same within the DU. BRI soil screening levels can be used for such an evaluation. In RTAs, in general military personnel are not exposed to a high extent to the MCs in the soil surface, at the exception of small arms range FP, where they very often lie down on the soil surface for aiming at the targets.

### **3.1.2 DU for protection of surface and groundwater**

Protecting the surface water and GW mandates that the source term of contaminant available to dissolution be carefully assessed, or the mean soil concentration of MC in the DU. The methodology and approach for protecting water bodies also requires as an input parameter the volume of contaminated soil. Surface water potential contamination mandates that all surface water bodies be included in the sampling design plan, and that DUs be integrated in any potentially contaminated surface soil up-gradient of the surface water body.

The source area when considering GW contamination can be very large and typically range from half an acre and may go up to 30 acres. DU as large as 30 acres are not possible and 100 to 200 m<sup>2</sup> DUs are recommended in the suspected source zone area.

### **3.1.3 DU for risk-based ecological soil screening levels**

DUs must be integrated in areas populated by sensitive known ecological receptors. When available, ecological soil screening levels for the specific receptors must be used, but in their absence, BRI soil screening guidelines are recommended. Specific ecological risk assessment might be needed to establish the resource that requires protection. Examples can be preferred habitats for endangered species or contaminant sensitive species, such as turtles. In such cases, DUs must be delineated in a few representative areas of the sensitive habitat.

## **3.2 Actual and historical records review**

The range control team are the key personnel to acquire the needed information about actual range activities. They can pinpoint the key target areas, firing position and UXO contaminated areas. The consultation of CFRIS (Canadian Forces Range Inventory System) can be a great tool to gather information on the intensity of live fire training that has pertained in the specific live fire ranges. Historical records review might also prove to be helpful to identify former range function and design, which might have evolved with time. As an example, an actual FP can be a former target impact area. Information of former UXO clearance activities might prove helpful in determining the areas where high UXO density was found and could have led to the dispersion of explosives from low order or UXO casing breaking.



### 3.3 Safety aspects/sampling in UXO contaminated sites

Sampling in RTAs represents a high safety risk as they are in general heavily impacted with UXOs. All the personnel involved in the sampling campaign need a mandatory safety briefing given by the range control office and everyone must sign a clearance document in which they testify that they had the safety brief and comply with the exposed safety rules. When entering a UXO contaminated range, the sampling team must always be accompanied by an experienced EOD specialist that will indicate the safe path for walking and driving. **In other words, field activities must be supervised by EOD personnel.** They will conduct a surface access survey before any activity can take place. The EOD specialist should survey all the areas to be sampled before granting access to the sampling team and remain in constant radio contact with Range Control to ensure that the location of the sampling team is well-known. In sampling RTAs, the sampling crew must always be aware that other live firing activities might happen elsewhere in the RTA and that they must always remain in the range where access was granted by the range control, and obtain permission before moving elsewhere in the RTA.

In heavily impacted ranges, the EOD must walk first in the impact area, and the person doing the soil sampling must walk in his footsteps. Only surface sampling (0-2 cm) using either scoops or corer (as will be presented later in section 3.3) can be conducted where no visual evidence of UXO or UXO large fragments are present. If no EOD is available from the RTA personnel, the sampling team must hire one from the private industry with a proven EOD expertise. In very high density UXO areas or in antitank impact area where piezoelectric fuses might be triggered only by the shade of a person, access might be either denied or restricted to the EOD only, who could perform the sampling after careful sampling instructions.

In some instances such as in grenade range where the soil profile is frequently tilled and mixed by the activity, sub-surface sampling might be of interest. This is also true at locations where high surface concentrations of MC are detected. Sub-surface sampling can be conducted only with the use of metal detector such as the one illustrated in Figure 23. The proofing metal sweep must be conducted regularly, at each 15 cm interval prior to digging any further. If metal is detected in the sub-surface sampling area, the location must be changed.

Small arms ranges are an exception to this as they do not generally contain unexploded ordnances (UXOs), so range clearance is not necessary for surface sampling (top 2 cm) and stop berms. Clearance should not be necessary for subsurface sampling, (below 2 cm) unless otherwise directed by range operations, as past activities conducted in these ranges might have involved higher calibers and UXO producing rounds.



*Figure 23. Metal detector for proofing prior to sub-surface sampling.*

### **3.4 Soil sampling**

Within any soil material there is inherent variability in chemical properties. The degree of variability differs according to numerous factors, including the size of the area, mode of contamination, the physical/chemical properties of the contaminant, and the soil type. These factors can produce spatial variability that is considerably larger than that encountered in other media. As discussed earlier, the dispersion of both organic and inorganic MC is highly heterogeneous. Adequate planning of the sampling program must occur in order to assure that samples represent the areas and depths desired, that sampling variability is properly determined and accounted for, and that there are sufficient numbers of samples at the appropriate locations to fulfill the purposes of the sampling. These considerations can be accounted for if specific objectives are defined early in the planning. In each specific firing range, the sampling plans include the location and size of the DUs in which multiple increments will be collected.

The delineation of the DUs, its size and location is the first step to soil sampling. Careful GPS recording of the DU limits are recorded to ensure that if needed, the same area can be sampled again in the future and for future references to the contaminant source zone. Flags shall be used to help the sampling process by giving visual indications to perform the systematic sampling pattern. Pictures of the area sampled shall be taken for any further need. As an example, in a rectangular 10 m<sup>2</sup> DU, flags of various colours can be placed at the limit of the DU at 1-m distance, to guide the person who will walk the DU in a serpentine manner.

#### **3.4.1 Soil sampling equipment**

As explained earlier, flags and GPS are needed for DU location and as sampling aids. MC are not volatiles and therefore polyethylene (PE) can be used for sample storage. Strong and large bags are needed, as 1-2 kg sample mass must be collected. Surface sampling can be performed with hardened plastic or metal scoops, spoons, or coring tools. A variety of sampling tools are

available to collect soil samples. They range from a spade to hydraulic powered coring equipment. Representative soil samples can best be obtained by using a core-sampling tool. The use of a proper sampling tool is essential for sampling to depths below 15 cm. The choice of collection tools often depends on the cohesiveness, coarseness and moisture content of the soil. Scoops and spoons are necessary for non-cohesive soils (such as sands) and heavily cobbled surfaces. Coring tools are recommended for cohesive surface soils with and without vegetation. Coring tools minimize surface disturbance and help maintain the consistency of the sampled surface area and depth. When shallow-depth sampling is necessary, a metal corer (stainless steel hand corer) that is manually pushed or driven into the ground can be used. Often mechanically driven sampling equipment will be necessary when sampling at depths greater than a meter. All the sampling equipment that comes into contact with the soil should be carefully washed between each sample, including duplicates, to avoid cross-contamination. This operation is performed by rinsing the equipment with distilled water, then acetone and then cleaning with clean paper towel. The sampling tools do not need to be cleaned between increments, since individual increments within a sampling are part of the same sample. Figure 24 and Figure 25 illustrate the soil sampling spoons or corer that can be used for soil sampling.



*Figure 24. Soil sampling metallic spoon.*



*Figure 25. Soil sampling corer.*

Coring devices that assure a uniform diameter core through the entire DU are preferred for sample collection. Most devices such as hand auger do not control the amount of material per increment and the risk of user bias is greater, thus causing variations in the sub-sample representativity from one sub-sample to another. Although their use may be unavoidable for coarse gravel or un-cohesive soils, such tools are not recommended. CRREL developed a coring tool specific to MC sampling in cohesive soils (Figure 25). It involved a soil plunger which can be adapted to vary the sampling depth, and the corer diameter can also be varied, depending on the sampling goals. The diameter of the core should be adapted to obtain a dry weight sample mass of 1 to 2 kg for the prescribed number of increments. The CRREL corer tip is made of stainless steel which keeps its sharpness for better results. The corer is almost mandatory in vegetation covered soils, as the spoons are highly inefficient in such situations. The corer cuts through the vegetation, reaches the soil and the core sample contains both the vegetation and soil layer. Vegetation must not be removed as it may contain a large proportion of crystalline solid MC particles. Another advantage of the use of the corer is the fact that the user does not have to bend at each increment, as the corer was designed to be operated in upright standing position. With his feet, the user applies a pressure to the corer lower handle which penetrates the soil profile and upon collection; the removal of the core sample is done by pushing the plunger, releasing the content of the corer into the sampling bag. A rubber hammer can be used to tap the plunger to release the content of the corer since in the long run; using the hands to tap the plunger may hurt the user especially if many increments are collected during the day. Usually, sampling with the corer in teams where one person uses the core tool and the other holds the sample bag and records the number of increment is the best approach. Using a clicker hand-held counting device to record the number of increments is recommended, as it is easy to lose track of counting. The number of increments collected shall always be noted both in the field log book and on the



sample bag. The CRREL corer design is available at DRDC and interested readers may contact the authors to get the blueprints or else corers can be built and shipped for environmental officers. A few corers have already been sent to some environmental officers.

Samples shall be collected in sufficient quantity to perform an adequate treatment and analysis. A quantity varying between 1 and 2 kg is recommended. As a rule of thumb, a 2-cm core needs 85 increments to reach 1 kg of soil and a 3-cm core needs 38 increments, assuming a dry soil density of 1.5 g/cc and a core length of 2.5 cm. The coring device allows the sampling at various diameter cores and also at various depths. In general, we recommend using the 3-cm diameter core at 2.0 or 3.0-cm deep depending on the site. The smaller 2-cm corer is needed for sandy soil, which would flow out of the wider diameter corers. The larger corer would only be used for sites where very large samples are desired, such as wide area assessment.

Samples shall be stored in a clean and new polyethylene bag. Each bag or container should be identified with the sample identifier (site number, sample location, sample number, depth, date, and sampler's initials) using a waterproof marker. **Splitting the sample in the field to reduce the volume sent for laboratory analysis is not recommended.** Samples are stored according to the indications in subsection 3.4.1 and are then sent or brought to a commercial laboratory for analysis.

#### **3.4.1.1 Subsurface sampling**

Whatever method is selected for collecting samples, care must be taken to ensure that samples from particular depth increments are not mixed with soil from other depths. Sub-surface sampling must always be done from the deepest layer to the shallowest one to avoid vertical cross-contamination, i.e. the hole is drilled completely before being sampled. Soil horizons displaying different properties should be sampled separately since they may behave very differently with respect to contaminant accumulation and movement. For sampling at depth, composite samples within each borehole should be obtained if feasible by combining soil over the specific depth increment or horizon being represented by the sample.

### **3.5 Sample processing and storage**

Sample processing is as important as the sampling itself as it will ensure whole sample representativeness. As stated earlier, the heterogeneous nature of MC mandates that care be taken in the careful homogenization of the MISS. The common procedure for most of the environmental samples is to send them to private laboratories for processing and analysis. In the case of energetic materials, as it will be described in details later, the main processing step is the extraction which is carried out using solvent. In order to minimize the amount of solvent used and to reduce the overall costs of purchase and disposal, only a small portion of the sample is extracted. A widespread practice in commercial laboratories is to scoop off a small portion of the sample from the container for drying and processing. In the case of samples containing EM, this practice leads to results that are not representative of the whole sample since the distribution of EM is heterogeneous both in the field and within the MISS. For example, particles of EM can settle to the bottom of the container during shipment and storage. Sub-sampling of a part of the sample in the original container is unreliable and must not be allowed. The goal of the sample processing that will be described in this section is to obtain a small sample (10 g) that represents

the several kg of soil in the decision unit. In other words, the proportions of all constituents, including EM should be the same in the small sample that will be extracted as they were in the decision unit.

### **3.5.1 Sample storage and maximum holding times**

The soil samples, once collected in the field are kept in the dark at 4°C until their arrival at the laboratory. All containers should be kept closed and sealed during storage. When possible, suspected highly contaminated samples should be kept separated from low-concentration samples. The maximum holding time (MHT) for samples containing humidity is 14 days. In order to extend the holding times, samples can be either frozen (extend the MHT to two months) or air-dried under a fume hood in the dark to avoid photo-degradation. Once they are dried, they can be kept at room temperature in the dark. According to the work of Hewitt [38], soil samples that were air-dried and grounded are stable for up to 53 days, and likely much longer. Many samples that were stored for more than a year were re-analyzed, and showed the same concentrations as originally, so, in theory, dried samples are stable indefinitely.

### **3.5.2 Energetic materials processing**

Air drying of the soil samples must be conducted in specific conditions that will not alter the contaminants of concern. Once the samples are dried, they need to be homogenised, to ensure that the subsample which will be analysed is representative of the collected sample. The homogenization methods aim at ensuring that the EM contamination is distributed evenly in the sample (usually the 1 kg collected in the field), so that the small (10 g) sub-sample that will be extracted and analyzed is representative of this whole sample, which is representative of the whole DU. There are two methods for homogenizing the collected samples: the acetone slurry method and the mechanical grinding method. The first method uses acetone to dissolve the EM compounds and redistribute them evenly on the soil particles, while the second method rely on mechanical grinding to reduce the size of the EM particles and fibres to the same size as the soil particles to ensure uniform dispersion. The two methods for sample homogenization will be described in this subsection: the acetone slurry and the grinding procedure. U.S. scientists highly recommend using the grinding procedure. However, most of the commercial Canadian laboratories, if not all of them, do not possess the needed equipment to process samples using grinding. The acetone slurry then represents a good compromise. The grinding method is superior to the slurry in some instances, such as when high levels of propellant residues are to be found, but in general it leads to an acceptable homogenization of the samples. A recuperation study will also be presented in the next sub-section, which demonstrates that the soil type might influence the choice of homogenization method.

#### **3.5.2.1 Air-drying**

Drying the sample is carried out by simply spreading the sample in a clean vessel and allowing it to air-dry at room temperature under the hood in the dark. Clean glass dish (20 × 20 × 6 cm) – Pyrex vessel type – can be used for samples of mass up to 1 kg (Figure 26). Metal sheets (cookie-sheet like) lined with an aluminum foil can also be used, unless aluminum analysis is needed (Figure 27). Care should be exercised when transferring the samples from the container to the drying support in order to avoid wrong sample identification or loss of material. At this point, the

whole sample is air-dried, including grass and other objects. The samples are left to dry either in a fume hood or in a ventilated box in the dark at room temperature ( $< 25^{\circ}\text{C}$ ) (see Figure 27 - used with permission from CRREL Laboratory, Hanover, NH and Figure 28). The duration depends on the humidity percentage of the sample, but 24 hours are usually enough. The ventilation in the hood or box should be minimal to avoid any particle movement from one sample to another, which would lead to cross-contamination. Drying stops microbial activity that could bio-transform the EM and allows the next processing steps to be performed more easily. The temperature should not be raised, in an oven for example, to accelerate the drying because some losses of analytes can occur by volatilisation, sublimation or thermal degradation.



*Figure 26. Sample transferred in a glass vessel for drying.*



*Figure 27. Soil samples drying on a lined metal sheet and multiple samples drying in a ventilated plastic box.*



*Figure 28. Samples under a hood for drying.*



### 3.5.2.2 Acetone slurry

The acetone slurry method is a simple and inexpensive method to homogenize soil samples. For this method, the sample is placed in a  $20 \times 20 \times 6$  cm glass dish levelled in a fume hood (if the sample was dried in a glass dish, the acetone slurry can be done directly in it, without sample transfer to another dish). Acetone is slowly poured onto the surface until the liquid entirely covers the soil. The slurry is then stirred for a couple of minutes using a clean metal spatula to allow full contact between acetone and the soil (Figure 29). The acetone is then allowed to evaporate **slowly** in a fume hood in the dark at room temperature. A pierced lid made of aluminum foil can be used to reduce the drying speed. Drying periods ranged between 4 and 18 hours, depending on the soil type. In the case of samples that contain a high concentration of gun propellant residues, a crust of NC can be formed on the surface after drying.



*Figure 29. Acetone slurry.*

After homogenization by acetone, the samples need to be sieved. Sieving is done using a 2 mm sieve (U.S. sieve size #10 or Tyler equivalent 9 Mesh). In a clean fume hood, the sample is transferred from the glass dish into the sieve (Figure 30), which is placed over a clean paper, aluminum foil or clean stainless steel bowl. The soil aggregates are broken by hand (new nitrile gloves used for each samples) or using a spatula. The NC crust, if any, is broken using a mortar and pestle to allow sieving (Figure 31). Since all operation may spread dust, only one sample at a time is to be present in the fume hood. The fine fraction ( $< 2$  mm) is transferred to an identified clean bag, sealed and kept until ready for further processing. The coarse fraction ( $> 2$  mm) is saved in the original bag used for sampling and kept for further analysis if deemed appropriate.



*Figure 30. Sieving and storing the dried sample.*



*Figure 31. Breaking of the NC crust with a mortar and pestle before sieving.*

After all these steps, all material (mortar, pestle, sieve, glass dish, metal spatula, interior of fume hood) must be washed thoroughly using soapy hot water (Micro-90 soap is recommended), rinsed with demineralised or de-ionized water and rinsed a second time with acetone. The gloves should also be changed to avoid cross-contamination. Complete drying should be allowed before processing the next sample.

### **3.5.2.3 Grinding procedure**

As presented earlier, for samples taken at a site where the soil presents a high portion of organic material, the detection of NG is underestimated when using the acetone slurry method. In this case, it is recommended to use the grinding method. The steps described here start after the samples have been air-dried. One sample is placed under a fume hood for sieving. This step might spread some particles in the hood, so only the sample to be processed should be in the hood at this time (Figure 32).



*Figure 32. Material needed for sieving before grinding.*

Wearing new nitrile gloves, the large chunks of the air-dried sample can be broken in the tray by hand. The sample can then be transferred into a 2-mm sieve (U.S. sieve size #10 or Tyler equivalent 9 Mesh) and sieved into a metal bowl or any other container (again, if metal analysis is needed on the sieved fraction, care should be exercised to minimise contact with metal surfaces) (Figure 33). Hard soil aggregates can be broken in the sieve using a stainless steel spoon.



*Figure 33. Sieving of dried soil with a #10 sieve.*



The fine fraction ( $< 2$  mm) is transferred into an identified clean plastic bag for further processing. The coarse fraction ( $> 2$  mm) can be kept in the original bag for further analysis if needed. It is possible that grass passes through the sieve; in this case it is left in the sample (Figure 34).



*Figure 34. Left: coarse fraction in the plastic bag, fine fraction in the bowl; Right: sieved fractions ready for identification and storage.*

If the sample cannot be sieved, for example for highly vegetated samples, the entire sample should then be extracted. Sieving of samples with a 2-mm mesh ensures that all high explosive particles are smaller than the detonation critical diameter. Sieving with another sieve size is not recommended.

Before sieving the next sample, the aluminum liner (if used) is discarded and all the other materials are washed (sieve, bowl, fume hood surface) using soapy hot water (Micro-90 soap is recommended), rinsed with demineralised or de-ionized water and a rinsed a second time with acetone. The gloves should also be changed to avoid cross-contamination. Complete drying should be allowed before processing the next sample.

The sieved soil is then homogenized using a ring mill. While the U.S. EPA does not endorse any specific manufacturer or piece of equipment, the specification of Method 8330b calls out a LabTech Essa LM-2 Ring Mill as the mill that was used to establish the standard (Figure 35 and Figure 36). The sample is put in an 800-cc dish and a hardened steel (low-chrome content) puck is added (Figure 37). In order to obtain maximum efficiency, a mass of approximately 500 g should be placed in the bowl. No less than 200 g should be used. Excessive mass will lead to uneven movements of the puck in the bowl and a reduction in the grinding efficiency, while an insufficient amount will lead to premature wear of the bowl. For low-density samples, 500 g will overfill the bowl. In that case the bowl should be filled to the first third before adding the puck. The patented puck used with the mill has a concave curved bottom surface to provide more contact between dish and puck, leading to good grinding performance. The puck also has an off-center, truncated hole through it to assist in the mixing of the sample to assure homogeneity. Again, metal contamination may occur during the grinding, so care should be taken when choosing the type of grinding accessories, knowing the future analyses to be performed. Grinding is carried out for 60-sec intervals, with at least a one-minute - ideally five minutes - cooling period between the cycles to avoid temperature rise and components volatilisation in the sample

[119]. Samples from impact areas that contain high explosives only are ground for one single cycle. Samples from firing positions and demolition ranges, which contain NC-based propellant residues, are grinded for five 60-sec cycles to pulverise the hard nitrocellulose fibres. For samples larger than 500 g, multiple batches are used and the final fine powder (which looks like flour) is mixed thoroughly on a clean aluminum foil sheet. The adherence of the soil on the bowl during grinding is an indication that the soil is not dry enough. The sample should then be returned in a glass dish or on a metal sheet to complete the drying according to the method described earlier and reground.



*Figure 35. LabTech Essa LM-2 Ring mill, opened and closed.*



*Figure 36. Insertion of the bowl in the pneumatic clamp.*



*Figure 37. Grinding steps: Empty dish and puck; puck on top of soil sample before grinding; removing the puck after grinding; ground soil.*

#### **3.5.2.4 Comparison of the two homogenization methods – recuperation study**

Laboratory tests were performed to verify if the two methods give the same results for various types of soils for the analysis of propellant residues. Due to the presence of nitrocellulose fibres, the extraction of EM from propellant residues (i.e. NG and 2,4-DNT) is more challenging than for high explosives (e.g. HMX and RDX from main charge explosives). Three different soil samples of two types (sandy soil and organic soil) were processed, and extractions were done on a set of samples prepared in the laboratory using uncontaminated soil from Valcartier training range and propellant grains of known composition. The concentrations of 2,4-DNT and NG in the spiked soils were ranging from 1 to 5000 ppm (mg/kg dry weight). The complete results will be published in a separate publication, and only the conclusions are presented herein.

The study showed that in the case of 2,4-DNT, the two extraction methods give statistically the same results. The recuperation percentage using the acetone slurry method was  $100 \pm 10\%$  for the extractions in the organic soils, while it was  $90 \pm 20$  for the sandy soils (both averaged over the complete concentration range (1 to 5000 ppm)). In the case of the grinding method, the recuperation percentage was  $100\% \pm 5$  for the organic soil and  $102\% \pm 1$  for the sandy soil.

In the case of NG, the grinding homogenization gives a better extraction and more reliable results. The recuperation percentage (calculated as an average over the concentration range from 1 to 5000 ppm of contamination) is  $110 \pm 10\%$  for the extractions in the organic soils (averaged over



the complete concentration range (1 to 5000 ppm)). In the case of the acetone slurry method, the extraction of NG from organic soils is  $60 \pm 20\%$ , while it is  $80 \pm 10\%$  for the sandy soils. The concentration of NG in organic soils is thus underestimated when the acetone slurry technique is used. The grinding process should then be preferred when a good precision is needed for NG in that kind of soil. Further tests have shown that it is possible to extract the remaining NG in the soil by repetitive extractions with acetonitrile, which demonstrates that there are no losses by volatilization during the slurry process as previously hypothesized, but a very strong binding between the NG and the NC in the propellants. The grinding reduces the particle size and breaks the fibers, thus allowing an easier extraction of NG from the NC fibres by the solvent. The acetone slurry method can still be used, while taking into account that specifically for NG, an under estimation of the NG content will occur for samples with propellant contamination. For other analytes (e.g. HMX and RDX), both methods lead to comparable results.

#### 3.5.2.5 Sub-sampling homogenized samples

Once the samples are homogenized, either by the acetone slurry or by the grinding procedure, a representative sub-sample is prepared. The goal here is to sample a 10-g sample for extraction with a minimum amount of solvent. This sub-sample should be representative of the whole sample collected, which is itself representative of the decision unit chosen for the site. The ground soil is spread out on a clean surface, such as an aluminum foil sheet and using a spatula a 30-increment sample is built using the systematic approach to obtain a 10-g sample (Figure 38). An identified tared small amber vial is used to collect the sub-sample and the exact mass of the sample is recorded. The vial should close hermetically and be large enough to accommodate 20 mL of solvent and a head space should remain to ensure sufficient agitation for complete extraction.



*Figure 38. Build-up of a 10-g sub-sample using a systematic approach (30-increment).*

### 3.5.2.6 Extraction of the sub-sample of homogenized soil

The extraction of the EM from the 10-g sub-sample is carried out by adding 20 mL of acetonitrile (high purity - Optima LC/MS grade solvent) directly in the amber vial used for sub-sampling, shaking vigorously the vial by hand and placing it in a cooled sonic bath for 18 h. Since the vials will be in contact with water, care should be taken for identification. Stickers might be lost due to soaking. Permanent ink identification on the vial and the lid is suggested. According to Walsh and Lambert, the extraction using a shaker table at 150 rpm for 18 h at room temperature gives equivalent results and is therefore a suitable substitute for the cooled sonic bath [119]. After extraction, the bottles are removed from the shaker table or the sonic bath, are shaken vigorously by hand one last time and are left to settle for 1 hour. A centrifuge can also be used at low revolution to accelerate the settling.

The particle-cleared liquid is withdrawn from the vial using a syringe. A disk filter (0.45- $\mu$ m pores) is fitted to the syringe and the solution is filtered into a clean vial, taking care to discard the first mL of liquid. This solution can be kept closed hermetically in the freezer if analysis cannot be performed right away and has a maximum holding time of one month.

### 3.5.3 Metals processing

Preparing samples for laboratory analysis is just as important as collecting the soil sample. As the distribution of metals in the soil samples is heterogeneous, it is essential to process the soil samples before their analysis. The purpose of sample treatment is to produce a smaller, dry and manageable sample suitable for laboratory scale analysis while at the same time ensuring that the prepared sample is homogeneous and fully representative of the original field material. The current practice of most commercial laboratories consists in collecting only 1 to 3 g of sample from the top of the soil container for analysis, often without performing homogenization. This practice does not provide representative results.

To obtain meaningful analytical results, it is imperative that sample preparation be done properly. First, the samples shall be dried at temperatures below 40°C to avoid the potential loss of volatile compounds, such as antimony, arsenic and mercury, and to avoid the oxidation of some heavy metal compounds, especially sulfides. To decrease the drying time and optimize the heat transfer, this operation shall be performed by placing the whole sample in large flat stainless steel or glass trays. The whole sample should then be sieved using stainless steel screens to remove pebbles, sticks and bullet fragments larger than 2 mm. Soil agglomerates are integral part of the fine soil fraction to be analyzed, and thus care shall be taken at this step to achieve their disaggregation into particles smaller than 2 mm. The whole sample shall then be ground using a ring pulveriser to decrease the particle size below 75 microns. Care should be exercised to choose a ring pulveriser that will not contaminate the sample with the analytes of interest.

As shown in Table 14, several types of commercial pulverisers are available (steel, zirconia, tungsten carbide, agate, ceramic, etc.). Each of those pulverisers will introduce various contaminants in the sample. The main constituent of steel pulverisers is iron (Fe); other constituents may also be added in minor concentration, such as chromium (Cr), manganese (Mn), molybdenum (Mo), and nickel (Ni). If the concentrations of these constituents in the samples are of concern in the analysis, then pulverisers made of other materials should be used instead, such as zirconia, tungsten carbide, agate or ceramic.

*Table 14. Pulverisation contaminants added by grinding equipment*

<b>Pulverizer material</b>	<b>Major contaminants</b>	<b>Minor contaminants</b>
Steel	Fe	Mn, Cr, Mo, Ni
Zirconia	Zr	Hf, Al
Tungsten carbide	W	Co, C, Ta, Nb, Ti
Agate	Si	Al, Na, Fe, K, Ca, Mg, Pb
Ceramic	Al	Ba

The concentration of contaminants introduced in the sample by the grinder will vary depending on the composition of the equipment, on the hardness of the grinding surface and of the sample, and on the duration of the grinding. Accredited laboratories shall provide detailed information about this operation and the associated contamination. In doubt, a clean sand sample obtained from a local supplier shall be sent to the laboratory for analysis with and without the pulverisation step.

## **3.6 Sample analysis**

The analysis for EM shall be done using High Pressure Liquid Chromatography (HPLC) while for metals it can be done either by Inductively Coupled Plasma (ICP) or X-Ray Fluorescence Spectrometry (XRF) (see sub-section 3.6.2.2 below). In relation to EM, section 3.5 is not intended to be an analytical training manual. The described methods are therefore written based on the assumption that they will be performed by trained analysts in chemical analysis, who are used to chromatography systems interpretation and experienced in the handling of explosive materials. This section does not address the safety issues associated with performing the various manipulations. The trade names and commercial products presented herein are for illustrative purposes only, and do not constitute a DRDC and DND endorsement or exclusive recommendation for use. The products and instrument settings cited represent those products and settings used during method development at DRDC Valcartier. Supplies, equipment, and settings other than those presented may be employed provided that method performance is appropriate for the intended application.

### **3.6.1 EM**

An aliquot of the extracted sample obtained as described in subsection 3.4.2.6 is collected for analysis. The filtered acetonitrile solution needs to be diluted with ultrapure water before injection in the HPLC system. The dilution varies depending on the HPLC system used, but at DRDC Valcartier, the optimization process confirmed that a 1:1 dilution gave the best results. An

automatic pipette can be used for this dilution. In the case of solutions with a high concentration of NC, a precipitate may appear. To avoid any plugging of the column, a filtration of this 1:1 solution using a 0.45 µm filter can be done before filling the HPLC vial. The samples prepared as described above are analyzed for energetic materials by HPLC using a dual wavelength ultraviolet (UV) detector. The prescribed method in the U.S. is the EPA Method 8330b [88]. The compounds included in the EPA Method 8330b are presented in Table 15.

*Table 15. Analytes detected with EPA Method 8330b.*

Analyte	Abbreviation	CAS* Number
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	HMX	2691-41-0
Hexahydro-1,3,5-trinitro-1,3,5-triazine	RDX	121-82-4
2,4,6-Trinitrotoluene	2,4,6-TNT	118-96-7
2,4-Dinitrotoluene	2,4-DNT	121-14-2
Nitroglycerin	NG	55-63-0
1,3,5-Trinitrobenzene	1,3,5-TNB	99-35-4
1,3-Dinitrobenzene	1,3-DNB	99-65-0
Methyl-2,4,6-trinitrophenylnitramine	Tetryl	479-45-8
Nitrobenzene	NB	98-95-3
4-Amino-2,6-dinitrotoluene	4-Am-DNT	19406-51-0
2-Amino-4,6-dinitrotoluene	2-Am-DNT	35572-78-2
2,6-Dinitrotoluene	2,6-DNT	606-20-2
2-Nitrotoluene	2-NT	88-72-2
3-Nitrotoluene	3-NT	99-08-1
4-Nitrotoluene	4-NT	99-99-0
Pentaerythritol tetranitrate	PETN	78-11-5
3,5-Dinitroaniline	3,5-DNA	618-87-1

CAS : Chemical Abstract Service Registry

Calibration of the HPLC system is carried out to ensure reliable quantification of the detected products. Individual and mixed stock standards of the target analytes needed to prepare the calibration curve for the analysis of EM are available from several commercial vendors, generally at a concentration of 1000 mg/L. Stock standards should remain refrigerated when not in use.

The concentrated solutions should be diluted prior to HPLC calibration. This dilution is performed considering that the final solution should be of the same solvent constituent as the sample, i.e. the solution should be 1:1 water:acetonitrile (half of the final volume is acetonitrile, the other half is water). For example, if a standard solution is to be prepared in a 10-mL volumetric flask, 5 mL of acetonitrile are added to the flask (this can be done using an automatic pipette) then the concentrated solution of EM is added and the flask is filled to the graduation line with ultrapure water. The final concentration of the solution in the flask is used to build the

calibration curve. A five-point calibration curve is recommended for EM determination. The calibration curve must be linear for the entire chosen domain.

A representative chromatogram obtained for a calibration solution with DRDC's system (25 ppm for all compounds, detection at 250 nm) is shown in Figure 39. The approximate retention times and the wavelengths used for all analytes detected in this method are presented in Table 16. The approximation in the retention times is due to the fact that they change with aging of the column, so they are presented for information only.

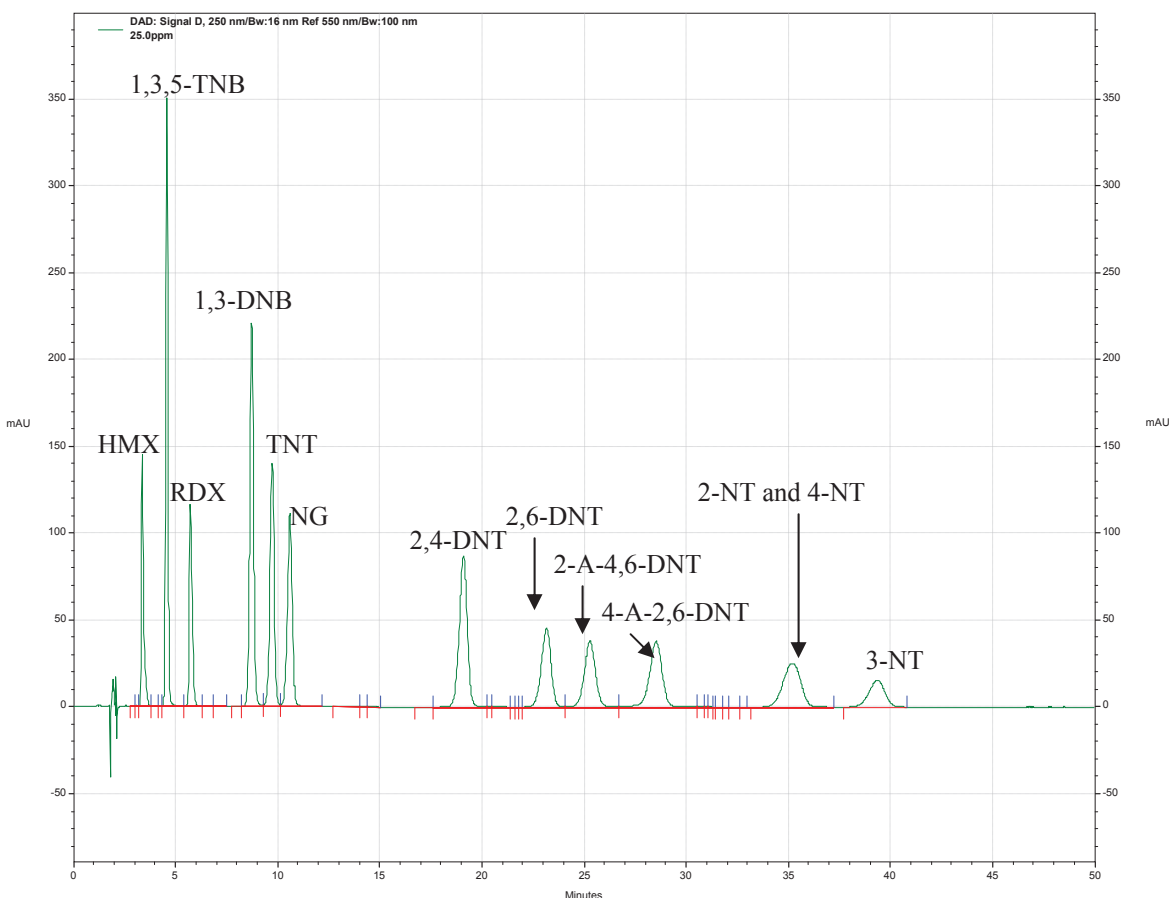


Figure 39. Chromatogram for a 25 ppm calibration solution of mixed EM, detection at 250 nm.

*Table 16:* Retention time and detection wavelength for analytes detected by HPLC (DRDC's HPLC system).

Analyte	Retention time (min)	Wavelength for detection (nm)
HMX	3.56	230
1,3,5-TNB	4.64	230
RDX	5.89	205
1,3-DNB	8.77	250
TNT	9.82	230
Tetryl	10.8	230
NG	13.6	205
2,4-DNT	19.1	250
2,6-DNT	23.12	205
2-A-4,6-DNT	25.4	230
4-A-2,6-DNT	28.6	230
2-NT and 4-NT	34.5	205
3-NT	38.7	205

During the analysis sequence, it is recommended to perform continuous calibration verification (CCV) to ensure that there is no drift in the signal and no carry-over of contaminants from one injection to another. In CCV, a solution of known concentration (within the calibration curve range) is injected in the HPLC preceded by the injection of an uncontaminated solution (solvent only). This is done every ten samples.

Since the concentration of the samples is known only after HPLC analysis, sometimes the concentrations are outside the range used for calibration. For example, if the calibration was carried out from 0 to 20 ppm and a solution presents a concentration of 69 ppm, this value cannot be reported with accuracy. A dilution of the solution should be performed to ensure that the concentration is within the range of the calibration curve, as well as a second injection in the HPLC system. The dilution factor can be calculated knowing the approximate concentration determined: for example, in the case presented previously, the 69 ppm solution should be diluted to a concentration close to 10 ppm (it is recommended to target the center of the calibration curve). A dilution factor of 6 can therefore be used. It is recommended to make a new solution using the particle-clear solution instead of diluting the liquid in the HPLC vial. Care should be taken to keep the acetonitrile dilution ratio (1:1). For example, in this case, a dilution could be: 100 µL of the extract (particle-clear solution), 500 µL of ultrapure water and 600 µL of acetonitrile. This solution is then filtered using a 0.45-µm pores disc filter and placed in an HPLC vial. For solutions with multiple contaminants, it is possible that only one component is outside the linear range (for example: a sample with low concentration of 2,4-DNT and high concentration of NG). In this case, the dilution is performed considering the NG concentration and the analysis is performed a second time. It is possible that in this case the concentration of 2,4-DNT falls below the detection limit of the method, so when reporting the results, the value for 2,4 DNT is reported using the first injection (no dilution) and the value for NG is reported using the second injection (with dilution).

### 3.6.2 Metals

The analysis of metallic species on a soil sample can either be performed on the extracts or directly on the solid sample. Usually, extracts provide the best detection limits, but are more time-consuming.

#### 3.6.2.1 Extraction of metals

The first step of the analysis consists in digesting a small portion (one to two grams) of the dried and homogenised sample for further analysis. Two digestion procedures are commonly used: partial or total digestion process. The choice of the appropriate method depends on the sampling objectives.

The partial digestion process, based on the general guidelines of EPA method 3050B [120], consists in dissolving almost all elements that could become environmentally available using various ratios of hydrogen chloride (HCl) and nitric acid (HNO<sub>3</sub>); hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is sometimes added. The partial digestion process performs generally well for most metals, but will lead to an underestimation of 10 to 20% in some cases. Several silicates, sulphides and oxides (e.g., alumina, titanium oxide, etc.) are not digested using this method. Hydrochloric acid (HCl) is added to improve the recovery of some metals, such as antimony, barium, lead, and silver. The use of a mixture of HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>, without HCl, is not recommended for RTAs samples, because of the significant underestimations of the concentrations encountered for some metals. In Canada, this partial digestion process (sometimes referred to as the aqua regia method or the two-acid method) is often performed using various mixtures (3:1 or 1:2) of HCl and HNO<sub>3</sub>, without H<sub>2</sub>O<sub>2</sub>. The use of a mixture containing HNO<sub>3</sub> in excess is preferred with samples containing organic matter or sulphides.

The total digestion procedure, based on EPA method 3052 [121], is performed by using hydrofluoric (HF) in addition to H<sub>2</sub>O<sub>2</sub>, HNO<sub>3</sub> and HCl during the extraction. The performance of the extraction is better with most analytes, especially silicates. However, some refractory sample matrix compounds, such as titanium oxides, alumina and some oxides, will still resist digestion. In Canada, this technique, sometimes referred to as the four-acid digestion method or the multi-acid digestion method, is based on the use of HF, HCl, HNO<sub>3</sub> and perchloric acid (HClO<sub>4</sub>). The use of this extraction technique is more appropriate than the partial digestion method when the type of heavy metal compounds (speciation) in the sample is unknown, which is the case for RTAs samples. The total digestion procedure is also appropriate to perform mass balances, e.g. to compare the input (number of bullets fired) and output (concentration of analytes leaching) of heavy metals in a stop berm of a small arms range.

However, the total digestion procedure may lead to an inaccurate determination of some analytes due to the formation of volatile species. Special care has to be taken for samples containing antimony, arsenic, boron, gold, uranium and chromium. It is impossible to analyse silicon using this method, because of the formation of silicon tetrafluoride, a gas at room temperature. To avoid the loss of volatiles, the digestion process has to be conducted in a closed vessel, using a microwave apparatus.



### 3.6.2.2 Chemical analysis

The analysis of the samples is generally performed on the extract using Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) or Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES) following the general guidelines of EPA methods 6020A [122] or 6010C [123], respectively. Generally ICP-MS is used to determine concentration levels in the parts per billion and below while the ICP-AES is used to determine levels in the parts per million and higher.

The chemical analysis of Sb can also be performed using Instrumental Neutron Activation Analysis (INAA), which is performed directly on the pulverized and dried sample, avoiding thus the digestion step and potential Sb losses.

Another useful chemical analysis technique is XRF. This analytical technique can be used either in the laboratory or as a portable instrument, according to the general guidelines outlined in EPA method 6200 [124]. This method allows the determination of the concentration of metallic species directly in the field. The detection limits on dry and ground samples are in the parts per million, slightly higher than those of ICP-AES. Because of the use of X-rays, the operation of this kind of instrument is regulated by Health Canada and requires the user to follow a course and obtain a permit from National Resources Canada. In addition, the apparatus must comply with the Radiation Emitting Device (RED) Act.

The leaching potential of metal and potential threat to groundwater can be estimated using the Synthetic Precipitation Leaching Procedure (SPLP), based on SW-846 EPA Method 1312 [125]. The objective of this method is to simulate the effect of acid rain on contaminated soil samples. A slightly acidic fluid (pH of 4.2) is used east of the Mississippi River which reflects the impact of air pollution due to heavy industrialization and coal utilization. An extraction solution of a higher pH (5.0) is used west of the Mississippi River, reflecting less industrialization and smaller population densities. Typically, 100-g soil samples are extracted in the presence of a mixture of sulphuric and nitric acids during 18 hours. The leachate is then filtered and analyzed using ICP-MS. The use of ICP-AES or any other analytical method is not recommended for SPLP test because of the low detection limits needed.

According to Townsend *et al.* [126], the leaching ability of metallic species can be influenced by the pH, the particle size, the occurrence of complexation with other chemicals (ligands), the liquid-to-solid ratio (L/S), the leaching (or contact) time, the kinetics, the redox conditions and the chemical speciation of pollutants of interest. The leaching tends to increase in the presence of ligands that will favour complexation, with a decrease of particle size as well as with an increase of the L/S ratio or the contact time. The lowest leaching occurs at approximately neutral pH, and tends to increase both in acidic and basic conditions. Redox conditions have an influence on the chemical speciation of metallic species, which in turn has an influence on the mobility of the species. For example, reducing conditions will favour the more mobile and more toxic trivalent arsenic ( $\text{As}^{3+}$ ) instead of its pentavalent equivalent ( $\text{As}^{5+}$ ).

Several studies have been performed to evaluate the significance of SPLP concentrations and to link this information either with the concentration of contaminants in pore water or with the groundwater contamination potential [127][128][129][126][130]. Technical limitations of SPLP include the use of a L/S ratio of 20, which is not representative of field conditions. In addition,

some leachate solutions can take much longer than the 18 h prescribed by the EPA method 1312 to reach equilibrium. An additional limitation of SPLP is related to the dilution factor that occurs during vertical migration of contaminants toward groundwater. Generally, the risk to groundwater contamination tends to decrease with increasing groundwater table depth, with a few exceptions (e.g., fractured rock). An attenuation factor also needs to be considered to take into account the distance between the source of contaminants and the potential receptors [131].

Although SPLP concentrations are not identical to the concentrations of contaminants in the pore water under the contaminated zone, results indicate that they should be representative of pore water concentration at very shallow depth [127]. Given the current state-of-the-art R&D, it is believed that SPLP in conjunction with the use of appropriate lysimeters can provide an early warning of potential migration of contaminants toward groundwater. The direct comparison of SPLP concentrations with groundwater criteria is the most conservative way of predicting the contamination potential and is therefore the recommended method. Research in this area is ongoing and improved guidelines should be issued in the near future.

The use of Toxicity Characteristic Leaching Procedure (TCLP, EPA method 1311 [132]), is not recommended. TCLP was shown to be inappropriate for shooting range soils because of the introduction of a significant bias in the leaching concentrations due to the complexation of lead by the buffer solution used to perform the extraction and inability of reaching equilibrium during the 18 h recommended by the procedure [127][129].

### **3.7 Quality assurance/Quality control**

Field sampling reproducibility of MISS should be subject to quality assurance (QA) and quality control (QC) requirements similar to those traditionally required to demonstrate laboratory analytical reproducibility. Field replicates provide a measure of the total error or variability of the data set. Field replicates for MISS are not split samples, but real field replicates independently collected using the same process of random systematic sampling. Similar concentrations or low %RDS field replicates indicate that the data are scientifically defensible and representative of the area sampled, and is the only mean by which confidence can be quantified. The sampling plan must provide for enough replicate QC sampling to obtain the required precision. As a general rule, it is recommended to collect triplicate MISS for at least 10% of all the DUs. Whenever possible, the triplicates should be collected by three teams to validate the absence of bias.

After the homogenization step, some portion of the MISS samples should be sub-sampled and analyzed in triplicate to ensure that the laboratory sub-sampling procedures are adequate to control both compositional and distributional heterogeneities (laboratory replicates). If a %RDS superior than 15% is observed, the homogenization step must be repeated or improved.

Energetic-spiked samples are not recommended on a routine basis, because 1-2 kg samples would need a relatively large amount of standard. However, a 10 g sub-sample after homogenization should be fortified with a known concentration of nitroaromatics and nitramines for every batch of samples collected in a specific geological formation. This laboratory control sample shall be made by weighing 10.00 g of soil and adding 1 mL of 10 ppm standard solution (8330b mix) and 1 mL of 10 ppm NG. After drying under a fume hood for one hour, the sample is extracted using 20 ml of acetonitrile.

Background samples (10% of the total number of samples) need to be collected in a site of the same representative geology than the DU samples. The processing and analysing method of the background samples shall be exactly the same as that of all the other samples. For the metals, background samples are used to determine if the source of a precise metallic compounds on a given area is anthropogenic or military. Extreme care must be taken to ensure that the background and RTAs samples are processed (i.e., total vs partial digestion) and analysed (i.e., ICP-MS vs ICP-AES) **by exactly the same way**, otherwise the comparison will be worthless. This is especially important to keep this factor in mind when performing multi-year characterization.

When using the acetone slurry homogenization method, sample blanks need to be extracted at regular intervals (e.g. every 20 samples) to ensure that the process does not bring cross-contamination. When using the grinding homogenization method, grinding blanks need to be run between every sample batches to ensure that the grinder cleaning process is sufficient to prevent cross-contamination. With samples containing malleable metals (e.g., Pb) that can smear on the walls of the apparatus, a cleaning of the grinder between each operation with clean sand is recommended. The conditions that lead to smearing of soft metals on the grinder walls are not clear at this stage. This could be related to the particle size of the metal being ground, the grinding cycle or the grinding time.

## **3.8 Requirements for contract laboratories**

### **3.8.1 EM**

There are many challenges for the laboratory that will be selected for sample treatment and analysis. The large sample mass, laboratory space needed for drying in the dark, suitable grinding equipment or acetone slurry equipment, representative sub-sampling procedures, decontamination, and dust control measures are amongst them. However, the production of scientifically defensible results requires that these challenges be met.

First of all, the laboratory needs to dry the whole sample, then manually thoroughly disaggregate and sieve the sample to remove the particles larger than 2 mm, which are not defined as soil. The entire sieved sample shall then be either ground or slurried. Then the homogenized samples must be sub-sampled (30 increments) to build the sample that will be further extracted.

In Canada, to the authors' knowledge, there are no commercial laboratories that are equipped with the appropriate grinding tools, designed for energetic materials. That is why the acetone slurry procedure was kept, even if in some cases it is proven to cause the under-estimation of NG. Hopefully, commercial laboratories will implement the grinding procedures, and both methods will be available.

### **3.8.2 Metals**

At the chosen laboratory, all samples shall be dried at 40°C and homogenized by a recognized splitting technique (e.g., coning and quartering). If SPLP is necessary, the samples shall be sieved through a 9.5-mm filter. A portion of each sample (300 g) shall be further sieved through

a 2-mm filter before the extraction and analysis. For surface samples and general bioavailability assessment, it is recommended to use the partial digestion method in conjunction with either ICP-MS or ICP-AES.

For highly contaminated areas, such as small arms ranges, where the evaluation of the risk of migration to groundwater with depth samples is required, the use of the total digestion technique in conjunction with ICP-MS is mandatory. In addition, the remaining 9.5-mm sieved sub-surface samples from depth intervals 0 to 30 cm shall be extracted by the SPLP procedure and analysed by ICP-MS. Lastly, the pH and the cation exchange capacity (CEC) of each area of concern have to be assessed, both on the surface of the soil and below ground surface.

## 4 Specific strategies designed for ranges

The sampling strategy must be developed in order to be cost-effective, lead to reproducible and scientifically defensible results with high confidence level (good reproducibility, low %RDS) and must not be user dependant. The DU size and locations shall be dependent of the characterization objectives as described in section 2.5. The following sections will briefly describe the major types of ranges that are encountered in Canadian RTAs, and suggest a common approach for where and how to sample. The suggested characterization approaches are for considerations while totally different approaches can still be proposed when deemed relevant.

Because the precise knowledge of the metallic compositions of the munitions is unknown, specific source terms cannot be calculated. However, previous results have shown that several metals exceed the background concentrations (see sub-sections below) and are thus related to military training. Of these, the metal analytes frequently exceeding the guidelines are Cu, Zn and Pb and, to a lesser extent, Sb, chromium (Cr) and nickel (Ni). However, each RTA generally has its own specificity, because of the unique composition of each munition allowed to be used in a given site. The next sub-sections will provide a description of the metallic contaminants detected at concentrations above background and above guidelines in the main CF RTAs. This enumeration should not be used as an exhaustive list of metallic contaminants. For example, some innocuous metals, such as sodium, potassium and calcium, are not included in this enumeration. A more thorough description can be found in references [7] to [38], which have been reviewed in [38].

Table 17 highlights the EM that were most frequently encountered in specific ranges in the past, while Table 18 illustrates the metals commonly detected in concentrations above ISQG in specific ranges.

*Table 17. EM commonly observed by Range type*

Type of Range	RDX	HMX	TNT	2,4-DNT	4ADNT	2ADNT	NG
Hand grenade	✓	✓	✓		✓	✓	
Antitank rocket range	✓	✓	✓	✓	✓	✓	✓
Artillery range	✓	✓	✓	✓			✓
Bombing range	✓		✓				
Demolition range	✓	✓		✓			✓
Small arms ranges				✓			✓

Table 18. Metals commonly observed by Range type

Type of Range	Pb	Cu	Zn	Sb	Cr	Ni	Cd
Hand grenade		✓	✓				✓
Antitank rocket range	✓	✓	✓		✓	✓	
Artillery range	✓	✓	✓				
Bombing range	✓	✓		✓			✓
Demolition range		✓	✓		✓		
Small arms ranges berms	✓	✓	✓	✓			

The following sections will describe where and how to place the DUs. All DU locations must be carefully recorded using GPS. When rectangular DUs are used, the four corners are recorded, while for circular DUs, the center and four points in the circular limits are recorded. If many concentric circles are used, then all limits are recorded. Please note that the suggested DUs are suggestions and are site specific. Judgment related to DU location and size should be applied for each specific site.

## 4.1 Grenade ranges

Hand grenade ranges are typically a few hectares or smaller in size, and are often divided into different throwing bays. The surface soil is normally sandy and non-vegetated or very poorly vegetated and heavily cratered. Grenades are thrown from a bay behind a concrete fortified shoulder height wall to shield personnel from the metal fragments on detonation. Craters that may have formed during operations may have been filled during range management or decommissioning operations. The main hand grenades used on these ranges are the M67 hand grenade and 40-mm rifle grenade. Both contains Comp B as the explosive filler, a mixture of RDX (with traces of HMX as impurity) (60%), TNT (39%) and wax (1%). The highest energetic residues are typically observed from 5 to 50 m from the throwing bay in the direction where the grenades are thrown. Thus, energetics may have been mixed in the soil profile. A typical hand grenade range is illustrated in Figure 40. When grenades function as intended, only forensic traces of EM are deposited, while low orders create high source of EM. Figure 41 presents a low order hand grenade that was encountered in a U.S. RTA.

Here are the parameters frequently encountered in grenade impact area:

- In front of the bunker from the throwing bay:
  - Low levels of RDX and TNT and their metabolites
  - Cu, Zn and Cd at concentrations higher than guidelines



- Arsenic (As), nickel (Ni) and Pb at concentrations above background
- Contamination occurs from UXOs and low orders
- Sub-surface contamination down to a depth of 30 cm

Rifle grenades are propelled by either single or double base propellant so 2,4-DNT and/or NG can be suspected in front of rifle grenade FP, up to 15 m. The recommended approach for rifle grenade firing position is the same as will be described in section 4.2 for antitank firing position, while only in front of the firing line.



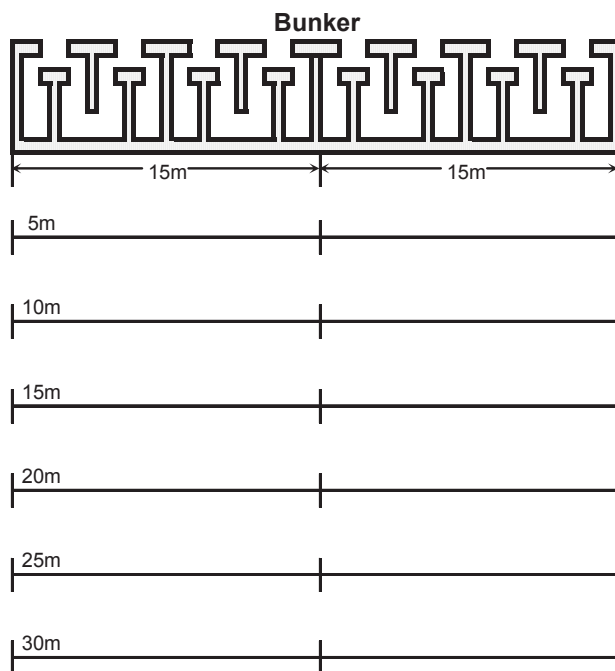
*Figure 40. Typical grenade range.*





*Figure 41. Low order hand grenade.*

The recommended approaches for grenade impact area are either to use the whole target impact area as a DU and collect at least 100 soil increment, or else to segregate the impact area in smaller rectangular areas if delineation of the contamination with distance from the throwing bay is sought after. Figure 42 illustrates an example where the impact area was delineated in 12 smaller DUs.



*Figure 42. Suggested DUs within a grenade impact area.*

Subsurface sampling up to 1 m deep can be done in a few locations, following section 3.2 guidance, as the soil profile of grenade range is frequently mixed by the detonation cratering.

## 4.2 Antitank ranges

These ranges are generally several hundred hectares in size and are covered with low vegetation due to the necessity of maintaining a direct line of sight between the firing points and the targets. On this type of site, projectiles are fired from shoulder-mounted tubes and are launched from a firing point hundreds of meters from the targets. Targets were usually old tanks, such as illustrated in Figure 43, that have been recently replaced by wooden targets, more environmentally friendly. The former use of old armoured vehicles has been stopped as it represents in itself a source of contaminants and when its service life as a target is over, it represents range scrap that is hard and costly to certify free from explosive for further disposal. New range design will address this specific issue.

The weapons mostly fired at the antitank ranges are the 66-mm M72 Light Armour Weapon (LAW) and the 84-mm Carl Gustav weapon. The 66-mm and the 84-mm Karl Gustav rockets have a warhead containing octol, a mixture of 70% HMX, and 30% TNT, as the main charge, with a booster containing RDX. The double base propellant used for these rockets contains mainly NG and NC as well as a small concentration of ammonium perchlorate in the M-72 propellant. Perchlorate being a highly soluble contaminant, it shall not be looked for in the soil surface while it should be included in the analyte set for antitank underlying groundwater quality evaluation. Antitank rockets have relatively high dud rate, leading to a high UXO density and to the spreading of their explosive content on the ground. These explosives can be dissolved by rain and water from snowmelt and can eventually infiltrate to the water table through the soil, thus contaminating the groundwater.

The highest concentrations of contaminants are generally encountered within a 20-m radius of each target and may reach levels as high as thousands of ppm of HMX. At the firing position, NG has been detected as far as 30 m in front and behind the firing line. Propellant residues (2,4-DNT and NG) have a very high residence time in the environment and have been measured at firing positions after more than 25 years of inactivity [62]. Firing positions therefore represent a high potential source term of NG while the target impact area generally presents high levels of HMX and metals, which have also a high environmental persistency due to their low solubility. Even if the explosive used contains TNT, it is always detected to lower levels than expected, mostly due to soil penetration and stabilization through irreversibly adsorbed metabolites.

Several metals (Cr, Cu, Ni, Pb, Zn) were detected at above-ISQG concentrations in soils of most of the CF anti-tank impact areas, generally close to the targets. In addition, Cd, Mo, Sb, As, silver (Ag), and strontium (Sr) were also detected at concentrations above background in impact areas. As, Cd, Mn, Mo and barium (Ba) were detected at above-background concentrations in firing positions. Cu and Pb were both detected in the groundwater and the surrounding water samples in concentrations exceeding the CCME guidelines.

Overall, the following can be expected at target impact area:

- HMX around targets up to 5000 mg/kg

- TNT rarely detected, at much lower levels than HMX
- RDX rarely detected
- Cr, Cu, Ni, Pb and Zn detected at above-ISQG concentrations
- Cu and Pb were both detected in the groundwater and the surrounding water samples in concentrations exceeding the CCME
- Cd, Mo, Sb, As, silver (Ag), and strontium (Sr) detected at concentrations above background in impact areas
- NG, As, Cd, Mn, Mo and barium (Ba) detected at above-background concentrations in firing positions.



*Figure 43. Typical antitank ranges and close view of a target tank.*

The recommended approach in antitank range target impact area is the establishment of circular DUs around each target, or around a representative number of targets. These can be done using only one large DU of 20 m radius with the target in the center using 100 MISS as illustrated in Figure 44, or else, 0-5 m, 5-10 m, 10-15 m, 15-20 m, 20-25 m circular sampling area, if the

delineation of the contamination with the distance from the target is relevant. Extreme care must be exercised when sampling around antitank targets, as the high dud rate and the extreme sensitivity of the antitank rocket UXO to stimuli bring a higher risk of detonation. Corer shall not be used in target impact area, as they penetrate in the soil profile. Sampling must be done using the sampling spoons with the collection of only the very surface soil layer (2 cm deep at the most).

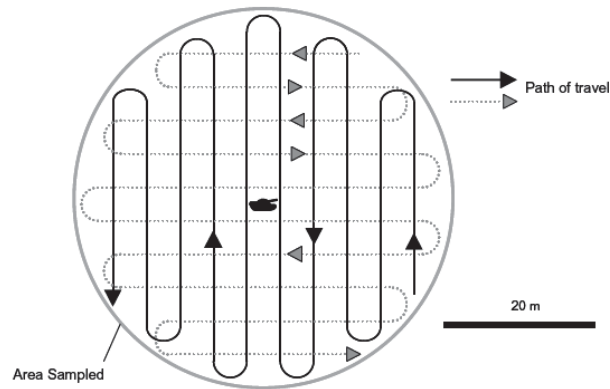


Figure 44. Suggested DU for an antitank target.

At the FP, the whole firing wall width must be sampled from the wall up to 30 m from the wall both in front and behind the firing line, as illustrated in Figure 45. Both rectangular DUs in front and behind the wall can be done in a whole using 100 MISS or else, could be sub-divided in smaller DUs (e.g. from 0-5, 5-10, 10-15, 15-20, and 20-30 m from the wall) if the discrimination of the levels of contaminants with distance from the wall is of interest.

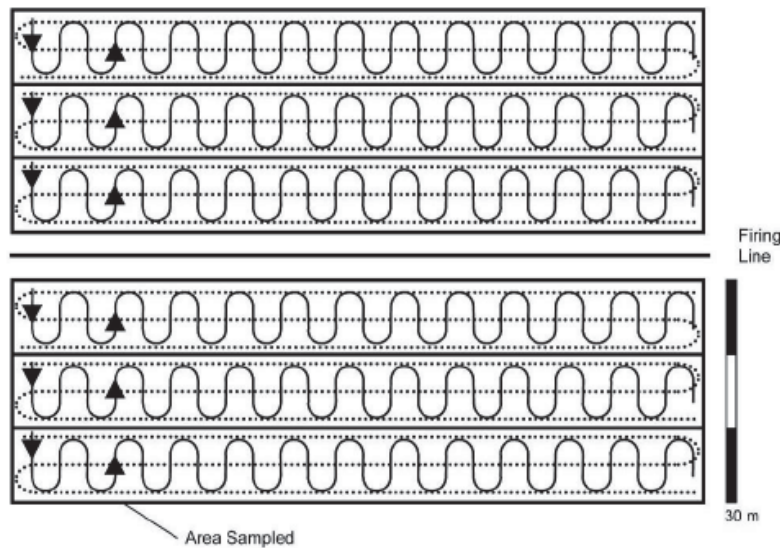


Figure 45. Suggested DUs for an antitank firing position.

### 4.3 Small arms ranges

Small arms training is a huge portion of the military activities: the Canadian Forces currently manages hundreds of active outdoor small arms ranges (SARs). All service personnel must indeed be qualified in the handling of a personal weapon. In Canada, millions of small calibre rounds are fired annually to maintain the CF troops in a high state of preparedness. This training has been increasing in the past years due to the numerous military operations abroad. In this context, small arms training ranges are being used extensively, which contributes to the escalation of residues accumulation on site, both at the firing positions and at the backstops in concentration high enough to impact the soil, biomass, surface water or groundwater [133][134]. At the firing positions, elevated concentrations of NG and 2,4-DNT were detected up to 8 m in front of the gun muzzles [60].

The recommended sampling pattern for the FP of SAR consists in collecting one sample per firing line. The whole line should be sampled using the systematic random sampling design. The sample should be built by collecting at least 50 increments of soils samples with the corer, up to 2 m in front of the firing line. As illustrated in Figure 46, the collection of increments should be performed by walking side-to-side and moving from one end to the other of the area of concern. For long firing lines, up to 100 sub-samples may be collected. This process should be repeated for each firing line, and at least one duplicate should be collected.

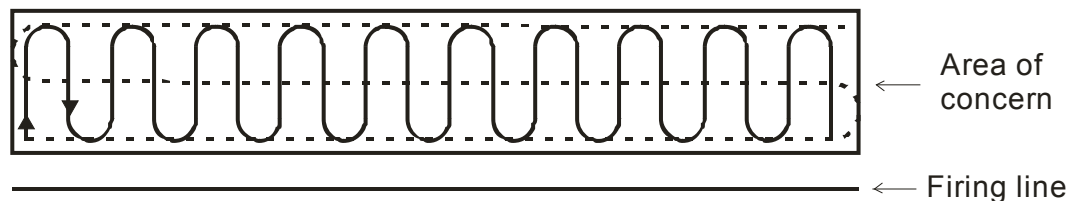


Figure 46. Typical sampling strategies for a SAR FP.

Contaminants of concern in the CF SARs are Pb, Cu and Sb in soils samples, which were detected in concentrations exceeding the CCME Industrial Soil Quality Guidelines (ISQG) for the Protection of Environmental and Human Health (PEHH). Pb and Sb were also sometimes detected in the groundwater above the Health Canada (HC) drinking water guidelines [135]. Other contaminants detected in above-background concentrations are Cu, Pb and arsenic (As) at the firing positions, and As, cadmium (Cd) and molybdenum (Mo) at the backstop berms. Elevated levels of Pb have also been found in vegetation growing near impact berms. Care must be taken to protect human health and the environment from lead's potential harmful effects.

Surface sampling of the top 2-cm soil of the backstop berm is recommended to evaluate the mean concentration of heavy metals. The necessary number of increments depends on the surface area sampled and on the local compositional heterogeneity. As for FP, the systematic random sampling design is recommended (Figure 46). However, the impact compartments or bullet pucks should be sampled separately, using a pattern similar to that of Figure 21. The collection



of 30 increments is an absolute minimum to obtain a statistically valid concentration. It is however recommended to collect approximately 50 to 100 increments for a group of three to four targets. The samples should be built by collecting at least 50 increments of soils samples within each DU with a garden spoon. Proper quality control is also essential to assess sample representativeness as well as to estimate the total uncertainty associated with a given sampling strategy and design, implying that replicate samples must be collected. It is recommended that 10% of the samples are collected in duplicate. An absolute minimum is one multi-increment sample per backstop berm. To avoid collecting co-located samples and to be random, each replicate of multi-increment samples should be collected starting at different locations of the area of concern.

As the flat area in front and behind the backstop berm can also be contaminated by heavy metals due to rainfall runoff, it is recommended to perform surface sampling of the top 2 cm to verify the presence of contaminants and better delineate the plume. As for the backstop berm, it is recommended to collect approximately 50 to 100 increments for a group of three to four targets.

Subsurface sampling is also recommended to verify the mobility of heavy metals in the soil. This operation can be performed by collecting core soil samples using a split spoon or pore water using lysimeters. The lysimeter method is advantageous because the pore water tends to drain a much larger area than core soil samples. However, the installation of lysimeters under the backstop berms is more expensive and more difficult than collecting samples with a coring tool. For these reasons, the installation of lysimeters is often performed when the backstop berm is rebuilt. When performed, core samples should be collected down to a depth of 1 m in the backstop berms and in the flat area in front of the backstop.

The following sub-section describes the suggested characterization protocol for a hypothetical 12-lane backstop berm, illustrated in Figure 47.

#### **4.3.1 Sampling strategy for a hypothetical 12-lane backstop berm**

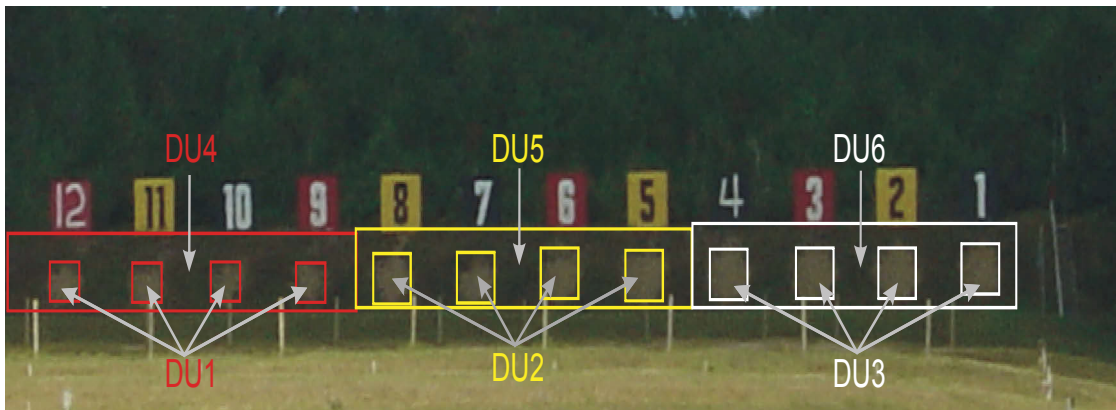
For example, in the 12-lane backstop berm illustrated in Figure 47, a minimum of eight surface samples would have to be collected. Three main areas of concern (AC) should be delineated:

1. The impact compartments (or bullet pockets, in the absence of impact compartments);
2. The area around the impact compartments (or bullet pockets, in the absence of impact compartments);
3. The flat area in front of the backstop berm

The areas of concern should be delineated by the bottom and the top of the berm, and its width should span to all targets. Each area of concern should then be sub-divided into DU that span approximately three to four targets. Thus, the characterization of the 12-lane backstop berm of Figure 47 will result in seven different DU:

1. Three DU in the impact compartments (DU1 to DU3)
2. Three DU around the impact compartments (DU4 to DU6)

3. One DU in the flat area in front of the backstop berm (DU7, now shown in Figure 47)



*Figure 47. Sampling pattern for a 12-lane backstop berm.*

The choice of three vs. four DU for this hypothetical berm is based on the presence of smaller bullet pockets for firing lanes 9 to 12, indicating a less extensive use. One surface sample per DU shall be collected, for a total of seven surface samples. In addition, for quality control and quality assurance (QA/QC), one to two additional samples shall be collected, one of them in the impact compartments (e.g., DU2). Thus, in the 12-lane berm, six surface samples (DU1 to DU6) should be collected directly in the berm. One additional surface samples should be collected in front of the berm (DU7). At least one duplicate should be collected, preferentially in the berm (DU2 dup). Thus, for a 12-lane backstop berm, the collection of at least eight surface soil samples is required. Each surface sample shall be built from the collection of at least 30 increments, and preferentially 50, using the systematic random sampling strategy (see Figure 21 and Figure 46). Care has to be taken during sampling to collect at least 300 g of dry sample of each surface soil.

If the evaluation of the potential mobility of metallic species toward groundwater is required, core samples need to be collected. A minimum of two to three core samples should be collected per AC. The core samples shall be collected in different DU (e.g., to build AC1 (0-15 cm), at least one core shall be collected in DU1, DU2 and DU3. In addition, if more than one core sample is collected per DU, different impact compartments shall be chosen. Lastly, for QA/QC, one to three additional core samples shall be collected in the AC suspected to have the highest contamination level.

Each core sample should be 1-m long and further divided into three to four sub-samples. Suggested depth intervals are the following: 0 to 15 cm, 15 to 30 cm, 30 to 60 cm, and 60 to 100 cm. Other depth intervals can be chosen to avoid mixing different soil formation (e.g. a sand top soil sitting on a clay formation). Care has to be taken during sampling to collect at least 300 g of dry sample of each of sub-surface soils from depth intervals 30 to 60 cm and 60 to 100 cm. In addition, a minimum of 500 g of sub-surface samples from depth intervals 0 to 15 cm and 15 to 30 cm has to be collected. The collection and combination of several sub-samples coming from the same depth interval will be required to achieve this amount of sample. The combination of the samples will thus result in four composite samples per AC per depth interval, for a total of 12



new samples: AC1 (0-15 cm), AC1 (15-30 cm), AC1 (30-60 cm), AC1 (60-100 cm), AC2 (0-15 cm), AC2 (15-30 cm), etc.

Lastly, a minimum of three background core samples shall be collected in clean areas close to the berm. The chosen sampling locations should be as representative as possible of the backstop berm soil formation. This step does not have to be repeated at each characterization, but has to be performed each time the soil formation is changed (e.g., rebuilt of the backstop berm). A good approach would be to grab three background core samples the first year, and then an additional one each year, that will be accounted for in the statistics.

Care has to be taken to carefully wash the sampling materials (scoop, auger) with diluted hydrochloric acid (10%) and distilled water between each sampling event. To avoid cross-contamination, sampling and sampling combination should begin by the less contaminated AC.

The net result of this 12-lane small arms range characterization is 28 samples: seven surface soil samples, one duplicate surface soil sample, 12 composite core samples (four composite core samples per AC), four duplicate composite core samples and four background composite core samples.

Also, additional samples will have to be collected for pH (1 sample per AC), cation exchange capacity (CEC; 1 sample per AC), Synthetic Precipitation Leaching Procedure (SPLP, 1 sample per AC) and grain size analysis (one sample from the stop berm).

#### **4.3.2 Analysis**

At the chosen laboratory, all samples shall be dried at 40°C, homogenized and split by a recognized technique (e.g., sample splitter, coning and quartering, etc.) and sieved through a 9.5-mm filter. A portion of each sample (300 g) shall be further sieved through a 2-mm filter, pulverized down to particles of 75 microns, extracted using a total digestion method, and analysed by ICP-MS. This will provide the total metal concentration of the surface soil of each DU and of the subsurface soil of each AC. The remaining 9.5-mm sieved subsurface samples from depth intervals 0 to 15 cm and 15 to 30 cm shall then be combined, extracted by the SPLP procedure and analysed by ICP-MS. These results will provide an indication of the potential mobility of the related contaminants. Lastly, the pH and the CEC of each area of concern have to be assessed, both on the surface of the soil and below ground surface.

The risk of groundwater contamination is based both on the mobility of contaminants and distance from the receptors. Low pH or CEC content increases the mobility of contaminants, which in turn increases the risk to groundwater contamination. Increases of the SPLP concentrations or of the total metal concentration indicate that the situation is deteriorating. The removal of the contaminated AC may be needed in the near future. Additional information may be needed on the site before taking this decision, such as the need for deeper aquifer sampling using a direct-push drill. Consultations should be undertaken with Director Land Environment and DRDC representatives to evaluate the situation and apply appropriate corrective measures.

Based on the information gathered so far, the following recommendations are made:

1. Shallow groundwater (less than 5 m)

In the presence of shallow groundwater (less than 5 m), the remediation of the contaminated AC should be planned as soon as possible if at least one of the following conditions is met:

- a. The SPLP concentration of any given contaminant exceeds the applicable drinking water criteria
- b. The concentration of contaminants in the core samples exceeds those of the background samples

In any other case, an annual monitoring of the surface and subsurface soil is recommended.

## 2. Deep groundwater (more than 5 m)

If the groundwater is deeper than 5 m, various situations may be encountered. An annual monitoring of the surface and sub-surface soil is recommended if at least one of the following conditions is met:

- a. The CEC is below 15 cmol/kg (15 meq/100 g)
- b. The pH is below 6 or higher than 9

An annual monitoring of the surface and subsurface soil, as well as additional investigations, such as the installation of lysimeters at various depths, are recommended if one of the following conditions is met:

- a. The SPLP concentration of any given contaminant exceeds the applicable drinking water criteria
- b. The concentration of contaminants in the core samples exceeds those of the background samples

In the absence of any alarming indicator, a regular monitoring is recommended. The frequency of monitoring will depend on the usage of the range and on the amount of precipitation. An annual follow-up is recommended in case of an increased usage of the range or an amount of precipitation significantly larger than the annual mean. Finally, in the presence of a stable situation, a follow-up is recommended every two to four years.

## 4.4 Artillery, mortar ranges, air-soil bombing ranges and battleruns

These ranges may cover several square kilometres to hundreds of square kilometres. In artillery and mortar ranges, firing positions are in general located around the circumference of the range with targets positioned near the centre of the range, as illustrated in Figure 48. Energetic contaminants have been observed up to 50 m downrange of firing points/areas for guns and within 25 m of each target. Ruptured UXOs and low orders represent the highest point source term.

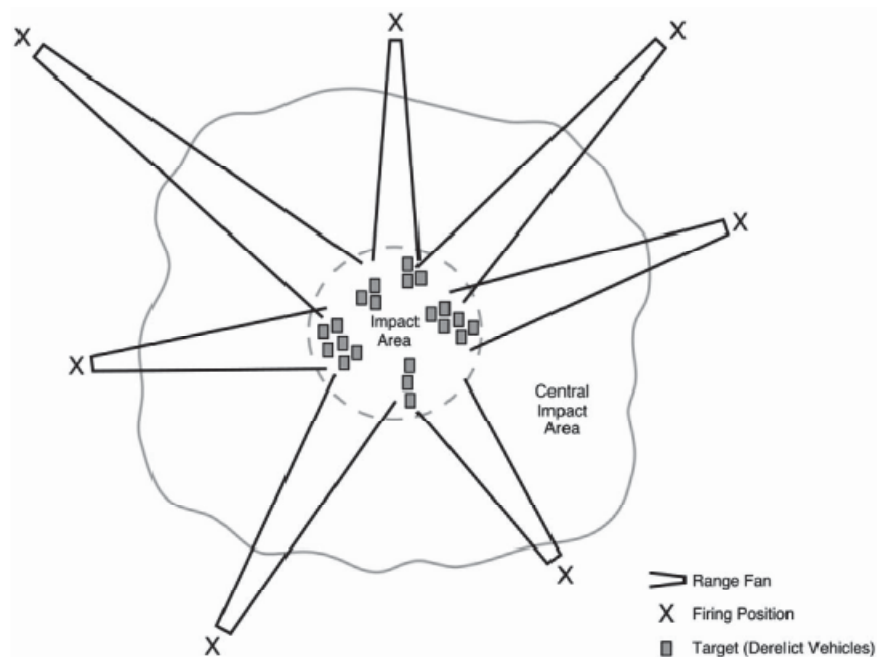


Figure 48. Illustration of an artillery firing range.

Once fired, artillery, mortar or tank rounds may travel several km before impacting the target areas. The flight path takes these rounds over an area referred to as the firing safety fan, where only a few defective rounds may end-up and detonate. When the detonation occurs as intended, this leads to a high order detonation that forms a crater upon impact, its size being related to the caliber of the round fired and based on the properties of the soil. Occasionally, rounds fail to detonate, creating a UXO that may be breached by other functioning round. The ammunitions mostly fired are artillery projectiles (105 and 155 mm), mortars (60 and 81 mm) and tank (105 mm). Most of the rounds fired are based on either TNT or Comp B, so the main contaminants in target impact areas are TNT and RDX. These rounds are propelled by either single, double or even triple base propellants, and therefore, at the firing positions, NG, 2,4-DNT and NQ are the potential contaminants of concern. Small arms may also be widely used in these large ranges, so metals shall be expected at target positions.

It is merely impossible to sample a representative surface of these wide ranges. Instead, high source terms must be looked for, such as targets, ruptured rounds and low order craters. When finding such source term, a DU of a size large enough to comprise the potential contaminants created by the source term needs to be done. Artillery ranges are indirect fire ranges and therefore the precision at target is lower than for direct fire ranges. It is thus recommended to use larger DUs at target. The same logic applies to air-to-ground bombing ranges. A suggested sampling pattern is illustrated in Figure 49.

DUs can also be delineated in heavily cratered areas, while in general, these are showing low levels of explosives residues. Figure 50 illustrates a potential pattern for DUs location. A large

DU encompasses the target impact area, while smaller DUs located within the largest one are positioned where source terms are observed.

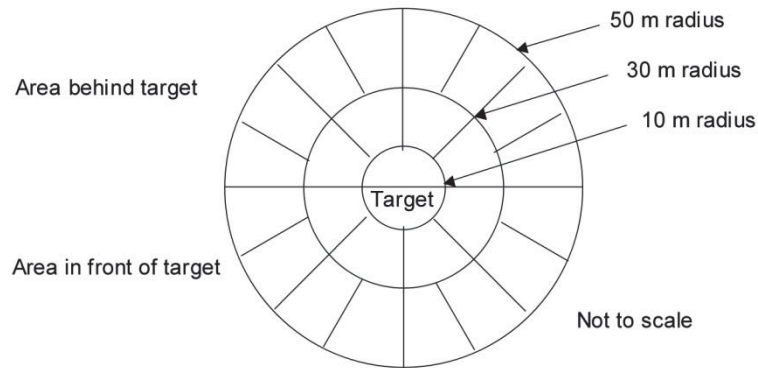


Figure 49. Suggested DU for an air-to-ground target.

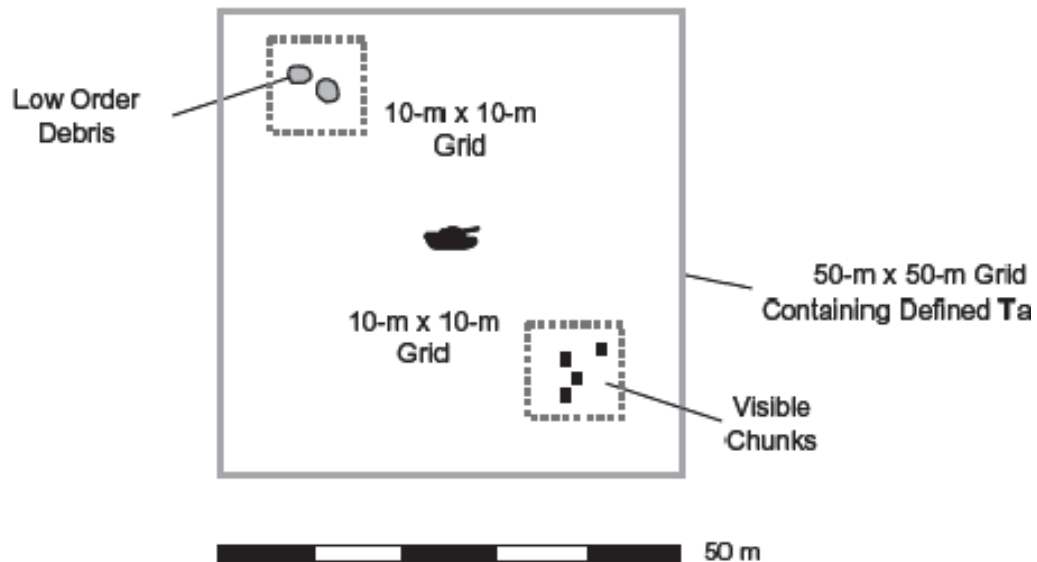


Figure 50. Proposed DUs for artillery/mortar impact areas or battle runs.

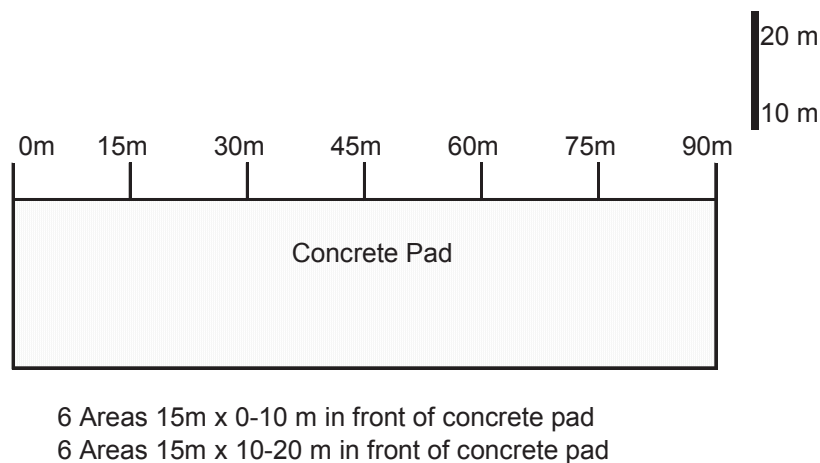
As stated earlier, firing positions might present measurable levels of propellant residues such as 2,4-DNT, NG and NQ. Whenever firing positions are known and identifiable, they must be sampled using square or rectangular DUs that would encompass the deposition area. For all these rounds, the deposition area is located directly in front of the firing position, and most of the

contaminants can be found in the first 20 m in front of the guns. Figure 51 illustrates a potential DU pattern that can be used when concrete firing pads are located at the firing position, such as in Meaford artillery range. The DU in this case could be as large as 90 m by 20 m, or else be subdivided in smaller DUs.

Mortar firing positions are more difficult to locate as mortars can be launched from almost anywhere in the range, while if identified, a DU of 10 x 10 m shall be sufficient.

The impact areas of artillery ranges and the battleruns are wide areas that should lead to a significant dispersion of contaminants. Nevertheless, Cu, Pb and Zn were detected at above-ISQG concentrations in several target areas of artillery ranges and battleruns. In addition, several metals were detected at concentrations exceeding the backgrounds, namely Sb, As, bismuth (Bi), Ni, Ag, Mo, Sr, Cd, and Cr. A similar situation was observed in firing positions, with Sb, Cu, Pb, Mo, Zn, Cd and cobalt (Co) at above-background concentrations. In artillery ranges, Sb (groundwater) and Cu (surface water) were detected at concentrations exceeding the CCME guidelines.

Finally, in artillery ranges, burn marks locations, caused by former field expedient burning of excess artillery propellants, shall be sampled and DU large enough to encompass all the burn mark plus 5 m in each direction shall be done. At these burn marks, 2,4-DNT and lead shall be looked for.



*Figure 51. Suggested DU in the firing position of artillery guns.*

## 4.5 Demolition ranges

Demolition ranges are generally a few hectares in size. They are used by the military EOD technicians to detonate various ammunition items that are considered safe to move. Military engineers also use extensively demolition ranges for the destruction of wooden, concrete and metallic structures using C4 explosive. C4 is mainly based on RDX, and it is the main EM of concern on these ranges. Figure 52 shows representative detonation bays and a demolition area

from demolition ranges. Small to large DUs must be placed in all active areas located within the demolition range. In general, large DUs of 20 m x 20 m can be placed in the larger wood cutting or steel cutting area, while smaller DUs can be placed in throwing bays and UXO demolition point. The best approach to locate the DUs in demolition ranges is to talk with the users, and figure out with them the most representative locations. Concentrations of energetic residues can be detected up to a depth of 4 m in soil in the areas where demolition and cratering were performed. Due to the various type of training in demolition ranges, and due to the fact that various munitions items can be open detonated there, a combination of many other energetic analytes might be expected. Multi-contamination by all explosives and propellant residues and heavy metal are to be expected. Cu, Zn and Cr are the main contaminants of concern in demolition ranges. The concentration of those contaminants exceeded the ISQG in most CF demolition ranges. Many other contaminants were also detected above background concentrations, including Sb, Pb, Fe, Ni, Mn, boron (B), Mo, Cd, Sr, Ag, As, Ba, tin (Sn), selenium (Se), and mercury (Hg).



*Figure 52. Representative detonation bays and wood cutting area.*

## 4.6 Wide area assessment

The characterization of wide impact areas (e.g., artillery, mortar, bombing ranges, etc.) is a major challenge because of the surface area of the site. Obtaining representative soil samples of whole RTAs or large portions of a site is not feasible. The usual approach consists in sampling areas of potential high contaminations, usually in the vicinity of targets, and in relying on hydrogeology to verify the presence of contaminants in groundwater and surface water. However, there may be cases where the source of contaminants may have to be more precisely delineated. For example, the leaching of contaminants out of the military training areas would mandate that the plume be managed appropriately, and the source of contamination located and removed. Unfortunately, this source of contaminants may not be in the vicinity of current targets, but could instead be a result of past training activities for which targets were either removed or destroyed. Ways to locate contaminated areas that don't have any noticeable points of interest are limited. One can rely on historic pictures of the site to understand how past military activities were performed and locate potential old targets. In addition, the direction of groundwater flow, provided by piezometric maps, can be extremely useful to determine the source of upstream contamination at a given observation well. Next, a rough delineation of the contaminated area can be performed



by collecting 100-increment samples using the random systematic sampling design (Figure 21) on 100-m x 100-m areas (i.e., one sub-sample per 100 m<sup>2</sup>). When contamination is detected, the contaminated areas can be more precisely delineated using the same sampling approach on smaller areas.

Extreme care has to be taken at all times to ensure the safety of the sampling teams, which should always follow the footsteps of qualified explosive ordnance specialists and see the area where they walk (e.g., avoid walking in long bushes, etc.). Scoops are preferred over corers, because of their smaller sampling depths.

## 5 Conclusion

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This guidance document is intended for future RTA soils surface characterization campaigns. It is based on a strong knowledge of MC deposition and fate. The most important parameters to minimize the cost and optimize the effectiveness of RTA characterization are as follows:

The following areas shall be considered potentially contaminated by propellant residues (contaminant of concern: NG, 2-4,DNT) in RTA's FP:

- In front of guns, from small arms to 155 mm calibers;
- Behind antitank rockets FP;
- At former excess propellant field expedient burning sites.

The following areas shall be considered potentially contaminated by explosive residues (Contaminant of concern: RDX, HMX, TNT) and heavy metals in RTAs' target impact areas (from lower to higher source of contamination):

- Cratered areas
- BIP locations
- Near targets
- Low orders locations
- Cracked UXO locations

The following items must be included in a statement of work to insure the success of RTA surface soil characterization:

- Include EOD personnel in all UXO contaminated site work for the safety of the sampling crew.
- The size and location of the decisions units (DUs) is judgmental, and planned using the knowledge sufficient to delineate areas that are likely to be contaminated, or likely to have differences in background concentrations or in variability. It shall be based both on past and future activities. It must also be closely linked to the sampling objectives identified in the early process.

Representative samples are the key to environmental characterization. Munitions constituents, mainly explosives, propellants and metals have shown a very high degree of compositional and distributional heterogeneities. In order to compensate that:

- DU must be carefully selected to respond to the sampling objectives and based on the live-fire activities.
- Compositional heterogeneity is controlled by sample mass/volume.
- Distributional heterogeneity is controlled by collecting many random increments.
- If the entire population is not well represented: under- or overestimation of the mass by orders of magnitudes can occur.
- High spatial distribution variability and compositional variability mandate that MISS be conducted. The number of increments and replicates are based on the size of the DU and the desired uncertainty level. When in doubt, the number of increments and replicates shall be maximized rather than minimized.
- Different ranges need different strategies.
- Uncertainties related to sampling and soil treatment greatly overcomes the precision of the analytical chemistry.
  - Soil samples of at least 1-2 kg must be collected using MISS within the DUs.
  - Careful sample homogenization using either the acetone slurry or grinding must be done. **The external laboratory must perform one of the homogenization process on the whole field sample.**
  - Using MISS and homogenization, field sampling variance shall be less than 30% RSD and laboratory sub-sampling variance less than 15 % RDS are expected.

The application of this protocol across Canada will ensure that contaminant sources in RTAs will be properly understood and identified and that remedial measures be undertaken whenever needed. It will allow the sustainable uses of our RTAs by the military troops. The knowledge acquired within many years of research is the basis of actual R&D dedicated to mitigate the contaminant sources. A burn table has been developed; a bullet catcher and greener munitions are also under development.

## References

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- [1] Environment Canada's Sustainable Development Strategy 2004-2006, Environment Canada, Ottawa, Canada. [http://www.ec.gc.ca/sd-dd\\_consult/SDS2004/index\\_e.cfm](http://www.ec.gc.ca/sd-dd_consult/SDS2004/index_e.cfm)
- [2] Fisheries Act (1985), Department of Justice, Ottawa, Canada. <http://laws.justice.gc.ca/en/showtdm/cs/F-14>
- [3] Canadian Environmental Protection Act (1999), Department of Justice, Ottawa, Canada. <http://laws.justice.gc.ca/en/c-15.31/>
- [4] Canadian Council of Ministers of the Environment (1999), Canadian Environmental Quality Guidelines, Ottawa, Canada. <http://documents.ccme.ca> (Access date, 25 April 2011)
- [5] Environment Canada (2011, Accelerated Reduction /Elimination of Toxics (ARET), , Ottawa, Canada, <http://www.ec.gc.ca/Publications/default.asp?lang=En&xml=A2A7F1B4-599A-47C3-BF0E-F075B8211D91&OrderPrint=847005F2-8F23-4DD2-B841-5E809846B054&OrderType=print>, (Access date, 25 April 2011)
- [6] Defense Environmental Network & Information Exchange (online), Office of the Under Secretary Deputy of Defense Installations and Environment, U.S. <http://www.denix.osd.mil/> (Access date: 8 Sept. 2008).
- [7] Thiboutot, S., Ampleman, G., Gagnon, A., Marois, A., Jenkins, T.F., Walsh, M.E., Thorne, P.G. and Ranney, T.A., Characterization of Antitank Firing Ranges at CFB Valcartier, WATC Wainwright and CFAD Dundurn, DREV R-9809, Defence Research Establishment Valcartier, Val-Bélair, QC, Canada.
- [8] Ampleman, G., Thiboutot, S., Gagnon, A., Marois, A., Martel, R. and Lefebvre, R., Study of the Impacts of OB/OD Activity on Soils and Groundwater at the Destruction Area in CFAD Dundurn, DREV R-9827, Defence Research Establishment Valcartier, Val-Bélair, QC, Canada.
- [9] Thiboutot, S., Ampleman, G., Lewis, J. and Brochu, S. (2001), Evaluation of Heavy Metals Contamination at CFAD Dundurn Resulting from Small-Arms Ammunition Incineration, DREV TR-2001-127, Defence Research Establishment Valcartier, Val-Bélair, QC, Canada.
- [10] Dubé, P., Ampleman, G., Thiboutot, S., Gagnon, A. and Marois, A. (1999), Characterization of Potentially Explosives-Contaminated Sites at CFB Gagetown, 14 Wing Greenwood and CFAD Bedford, DREV TR-1999-137, Defence Research Establishment Valcartier, Val-Bélair, QC, Canada.
- [11] Ampleman, G., Thiboutot, S., Désilets, S., Gagnon, A. and Marois, A., Evaluation of the Soils Contamination by Explosives at CFB Chilliwack and CFAD Rocky Point, DREV TR-2000-103, Defence Research Establishment Valcartier, Val-Bélair, QC, Canada.

- [12] Thiboutot, S., Ampleman, G., Gagnon, A. and Marois, A. (2000), Characterization of an Unexploded Ordnance Contaminated Range (Tracadie Range) For Potential Contamination by Energetic Materials, DREV TR 2000-102, Defence Research Establishment Valcartier, Val-Bélair, QC, Canada.
- [13] Thiboutot, S., Ampleman, G., Martel, R., Paradis, D., and Lefebvre, R. (2001), Environmental Characterization of Canadian Forces Base Shilo Training Area (Battleruns) following GATES Closure, DREV TR 2001-126, Defence Research Establishment Valcartier, Val-Bélair, QC, Canada.
- [14] Ampleman, G., Thiboutot, S., Martel, R., Lefebvre, R., Ranney, T., Jenkins, T.F., and Pennington, J., Evaluation of the Impacts of Live Fire Training at CFB Shilo (Final Report), DREV TR 2003-066, Defence Research Establishment Valcartier, Val-Bélair, QC, Canada.
- [15] Thiboutot, S., Ampleman, G., Hamel, A., Ballard, J.M., Martel, R., Lefebvre, R. and Downe S., Research on the Environmental Conditions of Groundwater and Surface Water Prevailing in the Training Area at CFB Gagetown, New Brunswick, DRDC Valcartier TR 2003-016, Defence Research and Development Canada–Valcartier, Québec, QC, Canada.
- [16] Thiboutot, S., Ampleman, Lewis, J., Faucher, D., Marois, A., Martel, R., Ballard, J.M., Downe S., Jenkins, T. and Hewitt, A. (2003), Environmental Conditions of Surface Soils and Biomass Prevailing in the Training Area at CFB Gagetown, New Brunswick. DRDC Valcartier TR 2003-152, Defence Research and Development Canada–Valcartier, Québec, QC, Canada.
- [17] Thiboutot, S., Ampleman, G., Marois, A., Gagnon, A., Bouchard, M., Hewitt, A., Jenkins, T., Walsh, M.E., and Bjella, K., Environmental Condition of Surface Soils, CFB Gagetown Training Area: Delineation of the Presence of Munitions Related Residues (Phase III, Final Report), DRDC Valcartier TR 2004-205, Defence Research and Development Canada–Valcartier, Québec, QC, Canada.
- [18] Marois, A., Gagnon, A., Thiboutot, S. and Ampleman, G., Caractérisation des sites de destruction d'explosifs, Base des Forces aériennes de Bagotville, DRDC Valcartier TR 2003-028, Recherche et développement pour la défense Canada - Valcartier, Québec, QC, Canada.
- [19] Ampleman, G., Thiboutot, S., Lewis, J., Marois, A., Jean, S., Gagnon, A., Bouchard, M., Jenkins, T. F., Hewitt, A. D., Pennington, J. C. and Ranney, T. A., Evaluation of the Contamination by Explosives in Soils, Biomass and Surface Water at Cold Lake Air Weapons Range (CLAWR), Alberta, Phase 1, DRDC Valcartier TR-2003-208, Defence Research and Development Canada – Valcartier, Québec, QC, Canada.
- [20] Ampleman, G., Thiboutot, S., Lewis, J., Marois, A., Gagnon, A., Bouchard, M., Jenkins, T. F., Ranney, T. A. and Pennington, J. C., Evaluation of the Contamination by Explosives and Metals in Soils, Vegetation, Surface Water and Sediment at Cold Lake Air Weapons Range (CLAWR), Alberta, Phase II Final Report, DRDC Valcartier TR 2004-204, Defence Research and Development Canada – Valcartier, Québec, QC, Canada.

- [21] Marois, A., Gagnon, A., Thiboutot, S. and Ampleman, G., Caractérisation des sols de surface dans les secteurs d'entraînement, Base des Forces Canadiennes, Valcartier, DRDC TR 2004-206, Recherche et développement pour la défense Canada - Valcartier, Québec, QC, Canada.
- [22] Thiboutot, S., Ampleman, G., Marois, A. and Gagnon, A., Caractérisation des sols de surface du champ de tir et secteurs d'entraînement de la Garnison Valcartier, DRDC Valcartier TR 2008-190, Recherche et développement pour la défense Canada - Valcartier, Québec, QC, Canada.
- [23] Diaz, E., Brochu, S., Thiboutot, S., Ampleman, G., Marois, A. and Gagnon, A. (2007), Energetic Materials and Metals Contamination at CFB/ASU Wainwright, Alberta. Phase I., DRDC Valcartier TR 2007-385, Defence Research and Development Canada - Valcartier, Québec, QC, Canada.
- [24] Ampleman, G., Thiboutot, S., Marois, A. and Gagnon, A., Evaluation of Soil Contamination by Explosives and Metals at the Land Force Central Area Training Centre (LFCA TC) Meaford, Ontario (Phase I), DRDC Valcartier TR 2008-390, Defence Research and Development Canada – Valcartier, Québec, QC, Canada.
- [25] Brochu, S., Diaz, E., Thiboutot, S., Ampleman, G., Marois, A., Gagnon, A., Hewitt, A.D., Bigl, S.R., Walsh, M.E., Walsh, M.R., Bjella, K., Ramsey, C.A., Taylor, S., Wingfors, H., Qvarfort, U., Karlsson, R.-M. and Ahlberg, M. Environmental Assessment of 100 Years of Military Training at Canadian Forces Base Petawawa: Phase 1 - Study of the Presence of Munitions-Related Residues in Soils and Vegetation of Main Ranges and Training Areas, DRDC Valcartier TR 2008-118, Defence Research and Development Canada – Valcartier, Québec, QC, Canada.
- [26] Jenkins, T.F., Walsh, M.E., Thorne, P.G., Thiboutot, S., Ampleman, G., Ranney, T.A. and Grant, C.L., Assessment of Sampling Error Associated with Collection and Analysis of Soil Samples at a Firing Range Contaminated with HMX, CRREL Special Report # 97-22, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, NH, U.S., 1997.
- [27] Ampleman, G., Thiboutot, S., Marois, A. and Gagnon, A., Surface Soil Characterization of Explosive and Metals at the Land Force Central Area Training Centre (LFCA TC) Meaford, Ontario (Phase II) Final report, DRDC Valcartier, TR 2009-218, Defence Research and Development Canada – Valcartier, Québec, QC, Canada.
- [28] Jenkins, T.F., Grant, C.L., Brar, G.S., Thorne, P.G., Schumacher, P.W. and Ranney, T.A., Assessment of Sampling Error Associated with the Collection and Analysis of Soil Samples at Explosives Contaminated Sites, *Field Analytical Chemistry & Technology*, 1(3), 151-163, 1997.
- [29] Jenkins, T.F., Walsh, M.E., Thorne, P.G., Miyares, P.H., Ranney, T.A., Grant C.L. and Esparza J., Site Characterization for Explosives Contamination at a Military Firing Range Impact Area, CRREL Special Report 98-9, U. S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH, U.S., 1998.



- [30] Jenkins, T.F., Grant, C.L., Walsh, M.E., Thorne, P.G., Thiboutot, S., Ampleman, G. and Ranney, T.A. (), Coping with Spatial Heterogeneity Effects on Sampling and Analysis at an HMX - Contaminated Antitank Firing Range, *Field Analytical Chemistry & Technology*, 3(1), 19-28, 1999.
- [31] Jenkins, T.F., Pennington, J.C., Ranney, T.A., Berry, T.E., Jr., Miyares, P.H., Walsh, M.E., Hewitt, A.D., Perron, N., Parker, L.V., Hayes, C.A., and Wahlgren, Maj. E., Characterization of Explosives Contamination at Military Firing Ranges, ERDC Technical Report TR-01-05, U. S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, NH, U.S., 2001.
- [32] Walsh, M.E., Ramsey, C.A. and Jenkins, T.F., The Effect of Particle Size Reduction by Grinding on Sub-Sampling Variance for Explosives Residues in Soil, *Chemosphere*, 49(10), 1267-1273, 2002.
- [33] Hewitt, A.D. and Walsh, M.E., On-site Processing and Subsampling of Surface Soils Samples for the Analysis of Explosives. ERDC TR-03-14, U.S. Army Engineer Research and Development Center, Hanover, NH, U.S., 2003.
- [34] Walsh, M.E., Collins, C.M., Hewitt, A.D., Walsh, M.R., Jenkins, T.F., Stark, J., Gelvin, A., Douglas, T.S., Perron, N., Lambert, D., Bailey, R. and Myers, K. (2004), Range Characterization Studies at Donnelly Training Area, Alaska: 2001 and 2002, ERDC/CRREL TR-04-3, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, NH, U.S.
- [35] Jenkins, T.F., Ranney, T.A., Hewitt, A.D., Walsh, M.E. and Bjella, K.L. (2004), Representative Sampling for Energetic Compounds at an Antitank Firing Range, ERDC/CRREL TR-04-7, U.S. Army Engineer Research and Development Center, Hanover, NH, U.S.
- [36] Walsh, M.E., Ramsey, C.A., Collins, C.M., Hewitt, A.D., Walsh, M.R., Bjella, K.L., Lambert, D.J. and Perron, N.M. (2005), Collection Methods and Laboratory Processing of Samples from Donnelly Training Area Firing Points, Alaska (2003), ERDC/CRREL TR-05-6, U.S. Army Engineer Research and Development Center, Hanover, NH, U.S.
- [37] Jenkins, T.F., Thiboutot, S., Ampleman, G., Hewitt, A.D., Walsh, M.E., Ranney, T.A., Ramsey, C.A., Grant, C.L., Collins, C.M., Brochu, S., Bigl, S.R. and Pennington, J.C. (2005), Identity and Distribution of Residues of Energetic Compounds at Military Live-Fire Training Ranges, ERDC/CRREL TR-05-10, U.S. Army Engineer Research and Development Center, Hanover, NH, U.S.
- [38] Hewitt, A., Bigl, S., Walsh, M.E., Brochu, S., Bjella, K., and Lambert D. (2007), Processing of Training Range Soils for the Analysis of Energetic Compounds, ERDC/CRREL TR-07-15, U.S. Army Engineer Research and Development Center, Hanover, NH, U.S.
- [39] Pantea, D., (2011) Army Bases Range and Training Area Characterization, Chief of Land Staff, Director Land Environment, Report submitted for external review.

- [40] Pennington, J.C., Jenkins, T.F., Brannon, J.M., Lynch, J., Ranney, T.A., Berry, J., Thomas E., Hayes, C.A., Miyares, P.H., Walsh, M.E., Hewitt, A.D., Perron, N. and Delfino, J.J. (2001), Distribution and Fate of Energetics on DoD Test and Training Ranges: Interim Report 1, ERDC TR-01-13, U.S. Army Engineer Research and Development Center, Vicksburg, MS, U.S.
- [41] Pennington, J.C., Jenkins, T.F., Ampleman, G., Thiboutot, S., Brannon, J.M., Lynch, J., Ranney, T.A., Stark, J.A., Walsh, M. E., Lewis, J., Hayes, C.A., Mirecki, J.E. Hewitt, A.D., Perron, N., Clausen, J. and Delfino, J.J. (2002), Distribution and Fate of Energetics on DoD Test and Training Ranges: Interim Report 2, ERDC TR-02-8, U. S. Army Engineer Research and Development Center, Environmental Laboratory, Vicksburg, MS, U.S.
- [42] Pennington, J.C., Jenkins, T.F., Ampleman, G., Thiboutot, S., Brannon, J.M., Lewis, J., Delaney, J.E., Clausen, J., Hewitt, A.D., Hollander, M.A., Hayes, C.A., Stark, J.A., Marois, A., Brochu, S., Dinh, H.Q., Lambert, D., Martel, R., Brousseau, P., Perron, N.M., Lefebvre, R., Davis, W., Ranney, T.A., Gauthier, C., Taylor, S., and Ballard, J.M. (2003), Distribution and Fate of Energetics on DoD Test and Training Ranges: Interim Report 3, ERDC TR-03-02, U. S. Army Engineer Research and Development Center, Environmental Laboratory, Vicksburg, MS, U.S.
- [43] Pennington, J.C., Jenkins, T.F., Thiboutot, S., Ampleman, G., Clausen, J., Hewitt, A.D., Lewis, J., Walsh, M.R., Walsh, M.E., Ranney, T.A., Silverblatt, B., Marois, A., Gagnon, A., Brousseau, P., Zufelt, J.E., Poe, K., Bouchard, M., Martel, R., Walker, D.D., Ramsey, C.A., Hayes, C., Yost, S.L., Bjella, K.L., Trépanier, L., Berry, T.E., Lambert, D., Dubé, P. and Perron, N.M. (2005), Distribution and Fate of Energetics on DoD Test and Training Ranges: Interim Report 5, ERDC TR-05-2, U.S. Army Engineer Research and Development Center, Vicksburg, MS, U.S.
- [44] Pennington, J.C., Jenkins, T.F., Ampleman, G., Thiboutot, S., Brannon, J., Clausen, J., Hewitt, A.D., Brochu, S., Dubé, P., Lewis, J., Ranney, T., Faucher, D., Gagnon, A., Stark, J., Brousseau, P., Price, C., Lambert, D., Marois, A., Bouchard, M., Walsh, M., Yost, S., Perron, M., Martel, R., Jean, S., Taylor, S., Hayes, C., Ballard, J., Walsh, M.E., Mirecki, J., Downe, S., Collins, N., Porter, B. and Richard, K. (2004), Distribution and Fate of Energetics on DoD Test and Training Ranges: Interim Report 4, ERDC/EL TR-04-4, U.S. Army Engineer Research and Development Center, Vicksburg, MS, U.S.
- [45] Pennington, J.C., Jenkins, T.F., Ampleman, G., Thiboutot, S., Hewitt, A.D., Brochu, S., Robb, J., Diaz, E., Lewis, J., Colby, H., Martel, R., Poe, K., Groff, K., Bjella, K., Ramsey, C.A., Hayes, C.A., Yost, S., Marois, A., Gagnon, A., Silverblatt, B., Crutcher, T., Harriz, K., Heisen, K., Bigl, S.R., Berry, J., Thomas E., Muzzin, J., Lambert, D. J., Bishop, M.J., Rice, B., Wojtas, M., Walsh, M.E., Walsh, M.R. and Taylor, S. (2006), Distribution and Fate of Energetics on DoD Test and Training Ranges: Interim Report 6, ERDC TR-06-12, U.S. Army Engineer Research and Development Center, Vicksburg, MS, U.S.
- [46] Pennington, J.C., Jenkins, T.F., Ampleman, G., Thiboutot, S., Brannon, J.M., Hewitt, A. D., Lewis, J., Brochu, S., Diaz, E., Walsh, M.R., Walsh, M.E., Taylor, S., Lynch, J.C., Clausen, J., Ranney, T.A., Ramsey, C.A., Hayes, C.A., Grant, C.L., Collins, C.M., Bigl, S.R., Yost, S. and Dontsova, K. (2006), Distribution and Fate of Energetics on DoD Test and Training

Ranges: Final Report, ERDC TR-06-13, U.S. Army Engineer Research and Development Center, Vicksburg, MS, U.S.

- [47] Jenkins, T.F., Pennington, J.C., Ampleman, G., Thiboutot, S., Walsh, M.R., Diaz, E., Dontsova, K., Hewitt, A.D., Walsh, M.E., Bigl, S.R., Taylor, S., MacMillan, D.K., Clausen, J.L., Lambert, D.J., Perron, N.M., Lapointe, M.-C., Brochu, S., Brassard, M., Stowe, R., Farinaccio, R., Gagnon, A., Marois, A., Gilbert, D., Faucher, D., Yost, S., Hayes, C., Ramsey, C.A., Rachow, R.J., Zufelt, J.E., Collins, C.M., Gelvin, A.B. and Saari, S.P. (2007), Characterization and Fate of Gun and Rocket Propellant Residues on Testing and Training Ranges: Interim Report 1, ERDC TR-07-1, U.S. Army Engineering Research and Development Center, Vicksburg, MS, U.S.
- [48] Jenkins, T.F., Bigl, S.R., Taylor, S., Walsh, M.R., Walsh, M.E., Hewitt, A.D., Fadden, J.L., Perron, N.M., Moors, V., Lambert, D., Bayley, R.N., Dontsova, K.M., Chappel, M.A., Pennington, J.C., Ampleman, G., Thiboutot, S., Faucher, D., Poulin, I., Brochu, S., Diaz, E., Marois, A., Fifield, L.N.R., Gagnon, A., Gamache, T., Gilbert, D., Tanguay, V., Melanson, L., Lapointe, M., Martel, R., Comeau, G., Ramsey, C. A., Quémérais, B. and Simunek, J. (2008), Characterization and Fate of Gun and Rocket Propellant Residues on Testing and Training Ranges: Final Report, ERDC TR-08-1, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, NH, U.S.
- [49] Ampleman, G. Thiboutot, S., Marois, A., Gagnon, A., Woods, P., Walsh, M.R., Walsh, M.E., Ramsey C. and Archambault, P. (2010), Evaluation of the Propellant Residues Emitted During the Live Firing of Triple Base Ammunition Using a British 155mm Howitzer Gun at CFB Suffield, Canada, DRDC TR-10-269, Defence Research and Development Canada – Valcartier, Québec, QC, Canada.
- [50] Poulin, I., Diaz, E., Quémérais, B. (2008), Airborne Contaminants in Two Antitank Weapons Back Blast Plume : Carl Gustav 84-mm and M72 66-mm, DRDC Valcartier TR 2008-242, Defence Research and Development Canada – Valcartier, Québec, QC, Canada.
- [51] Poulin, I., Diaz, E., Quémérais, B. (2008), Particulate Matter Emitted from the M777 Howitzer During Live Firing, DRDC Valcartier TR 2008-215, Defence Research and Development Canada – Valcartier, Québec, QC, Canada.
- [52] Thiboutot, S., Ampleman, G., Lapointe, M.C., Brochu, S., Brassard, M., Stowe, R., Farinaccio, R., Gagnon, A., Marois, A. and Gamache, T. (2008), Study of the Dispersion of Ammonium Perchlorate Following the Static Firing of MK-58 Rocket Motors, DRDC Valcartier TR 2008-240, Defence Research and Development Canada – Valcartier, Québec, QC, Canada.
- [53] Ampleman, G., Thiboutot, S., Marois, A., Gamache, T., Poulin, I., Quémérais, B. and Melanson, L. (2008), Analysis of Propellant Residues Emitted During 105-mm Howitzer Live Firing at the Muffler Installation in Nicolet, Lac St-Pierre, Canada, DRDC Valcartier TR 2007-514, Defence Research and Development Canada – Valcartier, Québec, QC, Canada.

- [54] Quémérais, B., Diaz, E., Poulin, I., Marois, A. (2008), Characterization of Atmospheric Emission Produced by Live Gun Firing : Test on the Carl Gustav Antitank 84-mm Weapon, DRDC Toronto TR 2007-103, Defence Research and Development Canada – Toronto, Toronto, ON, Canada.
- [55] Quémérais, B., Melanson, L., Ampleman, G., Thiboutot, S., Poulin, I. and Diaz, E. (2007), Characterization of Atmospheric Emissions During Live Gun Firing at the Muffler Installation in Nicolet, Lac St. Pierre, Canada: Test on Howitzer 105 mm, DRDC Toronto TR 2007-060, Defence Research and Development Canada – Toronto, Toronto, ON, Canada.
- [56] Poulin, I. and Diaz, E. (2008), Airborne Particulate Matter Emissions During Live Firing of LG1 Mark II 105-mm Howitzer, DRDC Valcartier TM 2007-297, Defence Research and Development Canada – Valcartier, Québec, QC, Canada.
- [57] Thiboutot, S., Ampleman, G., Marois, A., Gagnon, A., Gilbert, D., Tanguay, V. and Poulin, I. (2008), Deposition of Gun Propellant Residues from 84-mm Carl Gustav Rocket Firing, DRDC Valcartier TR 2007-408, Defence Research and Development Canada – Valcartier, Québec, QC, Canada.
- [58] Walsh, M.R., Walsh, M.E., Bigl, S.R., Perron, N.M., Lambert, D.J. and Hewitt, A.D. (2007), Propellant Residues Deposition from Small Arms Munitions, ERDC/CRREL TR-07-17, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, NH, U.S.
- [59] Walsh, M.R., Walsh, M.E., Thiboutot, S., Ampleman, G. and Bryant, G. (2009), Propellant Residues Deposition from Firing of AT4 Rockets, ERDC Report ERDC/CRREL TR-09-13, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, NH, U.S.
- [60] Brochu, S., Poulin, I., Faucher, D., Diaz, E. and Walsh, M.R. (2011), Combustion Residues of Small Calibre Ammunition - Characterisation of the Gases and Particles Emitted during Firing, DRDC Valcartier TR 2011-XXX, Defence Research and Development Canada – Valcartier, Québec, QC, Canada (in press).
- [61] Thiboutot, S., Ampleman, G., Marois, A., Gagnon, A. and Gilbert, D. (2009), Nitroglycerine Deposition from M-72 Antitank Rocket Firing, DRDC TR-2009-003, Defence Research and Development Canada – Valcartier, Québec, QC, Canada.
- [62] Thiboutot, S., Ampleman, G., Gagnon, A., Marois, A., Martel, R. and Bordeleau, G. (2010), Persistence and Fate of Nitroglycerin in Legacy Antitank Range, DRDC Valcartier TR 2010-059, Defence Research and Development Canada – Valcartier, Québec, QC, Canada .
- [63] Mailloux, M., Martel, R., Gabriel, U., Lefebvre, R., Thiboutot, S. and Ampleman, G. (2008), Hydrogeological Study of an Antitank Range, Journal of Environmental Quality, 37(4), 1468-1476.

- [64] Bordeleau, G., Savard, M., Martel, R., Ampleman, G. and Thiboutot, S. (2008), Determination of the Origin of Groundwater Nitrate at an Air Weapons Range Using the Dual Isotope Approach; *Contaminant Hydrogeology Journal*, 98(3-4), 97-105.
- [65] Martel, R., Mailloux, M., Gabriel, U., Lefebvre, R., Thiboutot, S. and Ampleman, G. (2009), Behavior of Energetic Materials in Groundwater and an Antitank Range, *Journal of Environmental Quality*, 38(1), 75-92.
- [66] Lewis, J., Martel, R., Trépanier, L., Ampleman, G. and Thiboutot, S. (2009), Quantifying the Transport of Energetic Materials in Unsaturated Sediments from Cracked Unexploded Ordnance, *Journal of Environmental Quality*, 38(6), 2229-2236.
- [67] Bordeleau, G., Martel, R., Ampleman, G., Thiboutot, S. and Jenkins, T.F. (2008) Environmental Impacts of Training Activities at an Air Weapons Range, *Journal of Environmental Quality*, 37(2), 308-317.
- [68] Bordeleau, G., Martel, R., Schäfer, D., Ampleman, G. and Thiboutot, S. (2007), Groundwater Flow and Contaminant Transport Modeling at an Air Weapon Range; *Environmental Geology*, 55(2), 385-396.
- [69] Robertson, T.J., Martel, R., Quan, D.M., Ampleman, G., Thiboutot, S., Jenkins, T. and Provatas, A. (2007), Fate and Transport of 2,4,6-Trinitrotoluene in Loams at a Former Explosives Factory; *Soil and Sediment Contamination*, 16(2), 159-179.
- [70] Martel, R., Robertson, T.J., Doan, M.Q., Thiboutot, S., Ampleman, G., Provatas, A. and Jenkins, T. (2007), 2,4,6-Trinitrotoluene in Soil and Groundwater Under a Waste Lagoon at the Former Explosives Factory Maribyrnong (EFM) Victoria, Australia, *Environmental Geology*, 53(6), 1249-1259.
- [71] Monteil-Rivera, F., Halasz, A., Groom, C., Zhao, J.S., Thiboutot, S., Ampleman, G. and Hawari, J. (2004), Fate and Transport of Explosives in the Environment: A Chemist's View, *Ecotoxicology of Explosives and Unexploded Ordnance*, EET Series Textbook, CRC Press Ed.
- [72] Zhao, J.-S., Fournier, D., Thiboutot, S., Ampleman, G., and Hawari, J. (2004), Biodegradation and Bioremediation of Explosives, in: *Soil Biology, Bioremediation, Phytoremediation and Natural Attenuation*, Ed A. Singh and O. Ward. Vol. 1, Springer-Verlag, pp. 55-80.
- [73] Halasz, A., Groom, C., Zhou, E. Paquet, L., Beaulieu, C., Deschamps, S., Corriveau, A., Thiboutot, S., Ampleman, G., Dubois, C. and Hawari, J. (2002), Detection of Explosives and Their Degradation Products in Soil Environments, *Journal of Chromatography A*, 963(1-2), 411-418.
- [74] Hawari, J., Beaudet, S., Halasz, A., Thiboutot, S. and Ampleman, G. (2000), Microbial Degradation of Explosives: Biotransformation Versus Mineralization, *Applied Microbiology and Biotechnology*, 54(5), 605-618.



- [75] Hawari, J., Halasz, A., Beaudet, S., Groom, C., Paquet, L., Rhofir, C., Ampleman, G. and Thiboutot, S. (2000), Characterization of Metabolites During Biodegradation of Hexahydro-1,3,5-Trinitro-1,3,5-Triazine (RDX) with Municipal Sludge, *Applied and Environmental Microbiology*, 66(6), 2652-2657.
- [76] Sarrazin, M., Doddard, S.G., Savard, K., Lachance, B., Robidoux, P.Y., Kuperman, R., Hawari, J., Ampleman, G., Thiboutot, S. and Sunahara, G. (2009), Accumulation of Hexahydro-1,3,5-Trinitro-1,3,5-Triazine by the Earthworm *Eisenia Andrei* in a Sandy Loam Soil, *Environmental Toxicology and Chemistry*, 28(10), 2125-2133.
- [77] Rocheleau, S., Lachance, B., Kuperman, R.G., Hawari, J., Thiboutot, S., Ampleman, G. and Sunahara, G. (2008), Toxicity and Uptake of Cyclic Nitramine Explosives in Ryegrass *Lolium Perenne*; *Environmental Pollution*, 156(1), 199-206.
- [78] Robidoux, P.Y., Svensen, C., Sarazin, M., Thiboutot, S., Ampleman, G., Hawari, J., Weeks, J.M. and Sunahara, G.I. (2005), Assessment of a 2,4,6-TNT Contaminated Site Using *Apporectodea Rosea* and *Eisenia Andrei* in Mesocosms, *Archives of Environmental Contamination and Toxicology*, 48, 56-67.
- [79] Doddard, S., Sunahara, G., Kuperman, R.G., Sarrazin, M., Gong, P., Ampleman, G., Thiboutot, S. and Hawari, J. (2005), Survival and Reproduction of Enchytraeid Worms, *Oligochaeta*, in Different Soil Types Amended with Energetic Cyclic Nitramines, *Environmental Toxicology and Chemistry*, 24(10), 2579-2587.
- [80] Sunahara, G., Lotufo, G., Kuperman, R., Hawari, J., Thiboutot, S. and Ampleman, G. (2009), *Ecotoxicology of Explosives*, CRC Press, Taylor and Francis Group, Montréal, ISBN 978-0-8493-2839-8.
- [81] Robidoux, P.Y., Lachance, B., Didillon, L., Dion, F.O. and Sunahara, G.I. (2006), Development of Ecological and Human Health Preliminary Soil Quality Guidelines for Energetic Materials to Ensure Training Sustainability of the Canadian Forces, NRC report # 45936, National Research Council of Canada, Montréal.
- [82] Thiboutot, S., Ampleman, G., Dubé, P., Hawari, J., Spencer, B. and Paquet, L. (1997), Protocol for the Characterization of Explosives Contaminated Sites, DREV-R-9721, Defence Research Establishment Valcartier, Val-Bélair, QC, Canada.
- [83] Thiboutot, S., Ampleman, G. and Hewitt, A. (2002), Guide for Characterization of Sites Contaminated with Energetic Materials, ERDC-CRREL TR-02-01, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, NH, U.S.
- [84] Thiboutot S., Ampleman G., Brochu S., Martel R., Sunahara, G., Hawari, J., Nicklin, S., Provatas, A., Pennington, J.C., Jenkins, T.F. and Hewitt, A. (2003), Protocol for Energetic Materials-Contaminated Sites Characterization, Volume 2, Final Report TTCP WPN-4 KTA 4-28, Quebec. <http://www.em-guidelines.org>.



- [85] Hewitt, A.D., Jenkins, T.F., Walsh, M.E. and Brochu, S. (2009), Environmental Security Technology Certification Program - Project ER-0628. Validation of Sampling Protocol and the Promulgation of Method Modifications for the Characterization of Energetic Residues on Military Testing and Training Ranges, ERDC/CRREL TR-09-6, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, NH, U.S.
- [86] Hewitt, A.D., Jenkins, T.F., Wash, M.E., Walsh, M.R., Bigl, S.R. and Ramsey, C.A. (2007), Protocol for Collection of Surface Soil Samples at Military Training and Testing Ranges for the Characterization of Energetic Munitions Constituents, ERDC/CRREL TR-07-10, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, NH, U.S.
- [87] Clausen, J.L., Scott, C., Cramer, R.J. (2007), Development of Environmental Data for Navy, Air Forces and Marine Munitions, ERDC/CRREL TR-07-7, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, NH, U.S.
- [88] U.S. Environmental Protection Agency (2006), Nitroaromatics, Nitramines and Nitrate Esters by High Performance Liquid Chromatography (HPLC), EPA SW-846 Method 8330B, Revision 2,, <http://www.epa.gov/epawaste/hazard/testmethods/pdfs/8330b.pdf> (Accessed 25 April 2011).
- [89] Voie, O., Stomseng, A., Johnse, A., Rossland, H.K., Karsrud, T., and Longva K. (2010), Veiler for Undersøkelse, Risikovurdering, Opprydning og Avhending av Skytebane og Ovingfelt (Protocol for Investigation, Risk Assessment, Cleanup and Disposal of Shooting Range and Training Area), Forsvaret Forskningsinstitutt/Norwegian Defence Research Establishment report # FFI 2010/00116 Kjeller.
- [90] SAIC Canada (2009), Environmental Site Sampling Protocol for UXO Legacy Sites, Department of National Defence Environment Site Sampling Protocol, Ottawa.
- [91] Bach, J.C., Conway, B.E., Mulligan, S.B., Watts, K.A. (2006), U.S. Army Environmental Center's Development of AP-42 Emission Factors for Munition Use, 15<sup>th</sup> International Emission Inventory Conference - Reinventing Inventories - New Ideas in New Orleans, New Orleans.
- [92] Dontsova, K.M., Pennington, J.C., Hayes, C., Simunek, J., and Williford, C.W. (2009), Dissolution and Transport of 2,4-DNT and 2,6-DNT from M1 Propellant in Soil, Chemosphere, 77(4), 597-603.
- [93] Martel, R., Lange, S., Côté, S., Ampleman, G. and Thiboutot, S. (2010), Fate and Behaviour of Energetic Material Residues in the Unsaturated Zone: Sand Columns and Dissolution Tests, INRS-ETE report # R-1161, Institut national de la recherche scientifique, Québec, QC, Canada.
- [94] Thiboutot, S., Ampleman, G., Kervarec, M., Cinq-Mars, A., Gagnon, A., Marois, A., Poulin I., Boucher, F., Lajoie R., Legault, K., Withwell, S., Sparks, T., Eng, J., Cartier, M. and

Archambault, P. (2011), Development of a Table for the Safe Burning of Excess Artillery Propellant Charge Bags”, DRDC TR-2010-254, Defence Research and Development Canada – Valcartier, Québec, QC, Canada, May 2011.

- [95] Pennington, J.C., Hayes, C., Yost, S., Crutcher, T., Betty, T.E., Clarke J.U. and Bishop, M.J. (2008), Explosive Residues from Blow-in-Place Detonations of Artillery Munitions, Soil and Sediments Contamination, 17(2), 163-180.
- [96] Pennington, J.C., Silverblatt, R., Poe, K., Hayes, C. and Yost, S. (2008), Explosive Residues from Low-Order Detonations of Heavy Artillery and Mortar Rounds, Soil and Sediments Contamination, 17(5), 533-546.
- [97] Taylor, S., Level, J. Walsh, M., Walsh, M.E., Bostick, B. and Packer, B., “Underground UXO: Are They a Significant Source of Explosives in Soil Compared to Low- and High-Order Detonations?”, USA ERDC, ERDC/CRREL Report TR 04-23, December 2004.
- [98] Brannon, J. and Pennington, J.C. (2002), Environmental Fate and Transport Process Descriptors for Explosives, ERDC Report TR-02-10, U.S. Army Engineer Research and Development Center, Vicksburg, MS, U.S.
- [99] Dontsova, K.M., Hayes, C., Pennington, J. and Porter, B. (2009), Sorption of High Explosives to Water-Dispersible Clay: Influence of Organic Carbon, Aluminosilicate Clay, and Extractable Iron, Journal of Environmental Quality, 38(4), 1458-1465.
- [100] U.S. EPA Integrated Risk Information Database (1993), 2,4,6-Trinitrotoluene, CASRN 118-96-7.
- [101] U.S. Department of Health and Human Services (1998), Toxicological Profile, 2,4- and 2,6-Dinitrotoluene, Agency for Toxic Substances and Disease Registry.
- [102] Agency for the Toxic Substances and Disease Registry (ATSDR) (1995), Toxicological Profile for RDX, U.S., Department of Health and Human Service, Atlanta, Georgia.
- [103] R&D Command, U.S. Army Medical Bioengineering Laboratory (1985), HMX: 14-Day Toxicity Study in Rats by Dietary Administration, AD-A171 597, Aberdeen.
- [104] NIOSH Pocket Guide to Chemical Hazards (2005), Nitroglycerine, IDLH Information, 2005, <http://www.cdc.gov/niosh/idlh/55630.html> (last consulted July 2011)
- [105] Regulations and Advisory Toxicological Profile – Perchlorates, [www.atsdr.cdc.gov/ToxProfiles/tp162-C8.pdf](http://www.atsdr.cdc.gov/ToxProfiles/tp162-C8.pdf), (last consulted July 2011)
- [106] Nordberg, G.F., Fowler, B.A., Nordberg, M. and Friberg, L.T., Editors (2007), Handbook on the Toxicology of Metals (Third Edition), Academic Press, Burlington.
- [107] CCME, Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health, in Canadian Environmental Quality Guidelines, Canadian Council of Ministers of the Environment (CCME)

- [108] Centre d'expertise en analyse environnementale du Québec (2010), Guide d'échantillonnage à des fins d'analyses environnementales, Cahier 5 – Échantillonnage des sols, [www.ceaeq.gouv.qc.ca/documents/publications/echantillonnage/solsC5.pdf](http://www.ceaeq.gouv.qc.ca/documents/publications/echantillonnage/solsC5.pdf) (consulté, juillet 2011).
- [109] Ontario Ministry of Environment and Energy Standards Development Branch (1996), Guidance on Sampling and Analytical Methods for Use at Contaminated Sites in Ontario, ISBN-0-7778-4056-1.
- [110] Taylor, S, Campbell, S., Perovich, L, Lever, J. and Pennington, J. (2006), Characteristics of Composition B Particles from Blow-in-Place Detonations, *Chemosphere*, 65(8), 1405-1413.
- [111] Keith, L.H. (1991), *Environmental Sampling and Analysis, a Practical Guide*, Lewis Publishers, ISBN 0-87371-381-8.
- [112] Hathaway, J.E. (2005), *Determining the Optimum Number of Increment in Composite Sampling*, Master of Science Thesis, Brigham, Young University, United Kingdom.
- [113] Jent, P.J., Richard, C., Callahan, C., Levenger, R.S and Ellis, E.R. (2006), How to Take a Truly Representative Environmental Sample, American Society of Civil Engineers, Proceedings of the 2006 GeoCongress, p. 1-6 DOI 10.1061/40803(187)13.
- [114] Esbensen, K.H. (2004), 50 Years of Pierre Gy's "Theory of Sampling"—WCSB1: a Tribute", *Chemometrics and Intelligent Laboratory Systems (Elsevier)* 74(1): 3–6, United States Environmental Protection Agency Environmental Sciences Division P.O. Box 93478 Las Vegas, NV 89193-3478, March 1999.
- [115] State of Alaska Department of Environmental Conservation (2009), Draft Guidance on Multi Increment Soil Sampling.
- [116] Hawaiian State Department of Health, Office of the Hazard Evaluation and Emergency Response (2008), Technical Guidance Document, Chapter 4: Soil Sampling Collection and Approaches, USA, <http://www.hawaiidoh.org/tgm.aspx>. (Last consulted July 2011)
- [117] Ramsey, C.A. and Hewitt, A. (2005), A Methodology for Assessing Sample Representativeness, *Environmental Forensics*, 6(1), 71-75.
- [118] Jenkins, T.F., Hewitt, A.D., Walsh, M.E., Ranney, T.A., Ramsey, C., Grant, C.L. and Bjella, K. (2005), Representative Sampling for Energetic Compounds at Military Training Ranges, *Environmental Forensics*, 6(1) 45-55.
- [119] Walsh, M.E and Lambert, D.J. (2006), Extraction Kinetics of Energetic Compounds from Training Ranges and Army Ammunition Plant Soils: Platform Shaker vs. Sonic Bath Methods, ERDC/CRREL TR-06-6, U.S. Army Corps of Engineers, Cold Regions Research and Engineering Laboratory, Hanover, NH, U.S.

- [120] EPA (1996), Acid Digestion of Sediments, Sludges and Soils, EPA SW-846 Method 3050B, Revision 2, U.S. Environmental Protection Agency (EPA), <http://www.epa.gov/epawaste/hazard/testmethods/pdfs/3050b.pdf>
- [121] EPA (1996), Microwave assisted acid digestion of siliceous and organically based matrices, EPA SW-846 Method 3052, Revision 0, U.S. Environmental Protection Agency (EPA), <http://www.epa.gov/epawaste/hazard/testmethods/pdfs/3052.pdf>
- [122] EPA (1994), Inductively Coupled Plasma – Mass Spectrometry, EPA SW-846 Method 6020A, Revision 0, U.S. Environmental Protection Agency (EPA), <http://www.epa.gov/epawaste/hazard/testmethods/pdfs/6020A.pdf>
- [123] EPA (2007), Inductively Coupled Plasma – Atomic Emission Spectrometry, EPA SW-846 Method 6010C, Revision 3, U.S. Environmental Protection Agency (EPA), <http://www.epa.gov/epawaste/hazard/testmethods/pdfs/6010C.pdf>
- [124] EPA (2007), Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediments, EPA SW-846 Method 6200, Revision 0, U.S. Environmental Protection Agency (EPA), <http://www.epa.gov/epawaste/hazard/testmethods/pdfs/6200.pdf>
- [125] EPA (1994), Synthetic Precipitation Leaching Procedure, EPA SW-846 Method 1312, Revision 0, U.S. Environmental Protection Agency (EPA), <http://www.epa.gov/epawaste/hazard/testmethods/pdfs/1312.pdf>
- [126] Townsend, T., Jang, Y.-C. and Tolaymat, T. (2003), A Guide to the Use of Leaching Tests in Solid Waste Management Decision Making, Report #03-01(A), Department of Environmental Engineering Sciences, University of Florida.
- [127] Laporte-Saumure, M., Martel, R. and Mercier, G. (2010), Pore water quality in the upper part of the vadose zone under an operating Canadian small arm firing range backstop berm, submitted to Soil and Sediment Contamination: An International Journal, submitted April 2011. Manuscript ID: BSSC-2011-0082.
- [128] Martel, R., Laporte-Saumure, M., Varfalvy, V., Francoeur-Leblond, N., Deschênes-Rancourt, C., Trépanier, L., Randiandelinoro, F.-H., Côté, S., Jacques, L., Castellazi, P. et Mercier, G. (2011), Recherche et développement sur le devenir environnemental des métaux dans les buttes de tir de petit calibre, Rapport de recherche no. R-1253, Institut National de la Recherche Scientifique – Centre Eau Terre et Environnement.
- [129] Cao, X. and Dermatas, D. (2008), Evaluating the Applicability of Regulatory Leaching Tests for Assessing Lead Leachability in Contaminated Shooting Range Soils, Environ Monit Assess, 139, 1-13.

- [130] Townsend, T., Dubey, B. and Tolaymat, T. (2006), Interpretation of Synthetic Precipitation Leaching Procedure (SPLP) Results for Assessing Risk to Groundwater from Land-Applied Granular Waste, *Envir. Eng. Sci.*, 23, 239.
- [131] New Jersey Department of Environmental Protection (2008), Guidance for the Determination of Dilution Attenuation Factor for the Impact to Ground Water Pathway
- [132] EPA (1992), Toxicity Characteristic Leaching Procedure, EPA SW-846 Method 1311, Revision 0, U.S. Environmental Protection Agency (EPA), <http://www.epa.gov/epawaste/hazard/testmethods/pdfs/1311.pdf>
- [133] ITRC Small Arms Firing Range Team (2003), Characterization and Remediation of Soils at Closed Small Arms Firing Ranges, Interstate Technology and Regulatory Council, Washington D.C., USA, [http://www.itrcweb.org/gd\\_smart.asp](http://www.itrcweb.org/gd_smart.asp), (consulted July 2011).
- [134] ITRC Small Arms Firing Range Team (2005), Environmental Management at Operating Outdoor Small Arms Firing Range, Interstate Technology and Regulatory Council, Washington D.C., USA, [http://www.itrcweb.org/gd\\_smart.asp](http://www.itrcweb.org/gd_smart.asp), (consulted July 2011).
- [135] Health Canada, Guidelines for Canadian Drinking Water Quality, [http://www.hc-sc.gc.ca/ewh-semt/pubs/water-eau/index-eng.php#tech\\_doc](http://www.hc-sc.gc.ca/ewh-semt/pubs/water-eau/index-eng.php#tech_doc), (consulted July 2011)
- [136] Laporte-Saumure, M., Mercier, G. et Martel, R. (2006), L'évaluation de la composition et des propriétés chimiques et physiques des sédiments des buttes de tir - Étape I, Rapport de recherche R-850, Institut national de la recherche scientifique, Centre Eau, Terre et Environnement, Québec, QC, Canada.

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## **Annex A   Soil sampling equipment**

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Notebook (all-weather writing paper is recommended) with pencil/pen

Camera

GPS

Measuring tapes (100 m)

Flags of various colours

Sampling spoons

Sampling corers

Strong large polyethylene sampling bags (large enough for 1-2 kg soil samples)

Strong larger polyethylene bags (large enough for 7-8 kg of soils in case of wide area assessments)

Tie wraps or other system to seal bags

Sample tags

Permanent ink markers

Acetone sprayers

Distilled water

Paper towels (e.g. Kimwipes)

Gloves – latex or nitrile

Garbage bags for disposal of paper towels and gloves

Containers for sample storage -coolers with ice packs. Caution if using regular ice: make sure that it is in a sealed bag to avoid flooding of samples.

Clicker hand-held counting device

## Annex B Metal analytes and detection limits

*Table 19. Detection limits (d) for metals by in soil and in water by Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS), and CCME Industrial Soil Quality Guidelines (ISQG).*

Analyte	Symbol	d soils mg/kg	ISQG mg/kg
Aluminum	Al	4.0	NA
Antimony	Sb	1,0	40
Arsenic	As	1.0	12
Barium	Ba	0.1	2000
Beryllium	Be	0.1	8
Bismuth	Bi	2.3	NA
Boron	B	0.5	NA
Cadmium	Cd	0.3	22
Calcium	Ca	4.0	NA
Chromium	Cr	0.5	87
Cobalt	Co	0.5	300
Copper	Cu	0.4	91
Iron	Fe	0.6	NA
Lead	Pb	2.5	600
Lithium	Li	2.0	NA
Magnesium	Mg	0.3	NA
Manganese	Mn	0.15	NA
Mercury	Hg	NA	NA
Molybdenum	Mo	0.6	40
Nickel	Ni	1.0	50
Potassium	K	100.0	NA
Selenium	Se	1.0	3,9
Silver	Ag	0.7	40
Sodium	Na	9.0	NA
Strontium	Sr	0.3	NA
Tellurium	Te	0.2	NA
Tin	Sn	1.8	300
Uranium	U	NA	NA
Vanadium	V	0.3	130
Zinc	Zn	0.3	360

## **Annex C    Generic statement of work**

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The following information is provided to managers of Range and Training Areas to assist in the development of statements of work for requests for proposals.

### **Scope**

Development of a Soil Sampling Plan to assess the presence of munitions constituents in RTAs. The soil sampling plan must be approved by the environmental officer and the analysis of samples must be carried out by the Canadian Association for laboratory Accreditation (CALA) accredited laboratory to Method 8330B for energetics and ICP/MS method for metals.

The soil sampling involves the collection and analysis of soil samples from the terrestrial environment to determine the presence and concentrations of munitions constituents from decision units where anomalies related to munitions constituents are suspected. Soil sampling in dud producing munitions areas is to be conducted only under the direct supervision of appropriate Explosive Ordnances Disposal (EOD) expert personnel. The soil sampling strategy should be consistent with Defence Research and Development Canada guidance document (DRDC Report TR 2011-447) for Range and Training Areas (RTA). Soil sampling should consist of multi-increment systematic random sampling within decision units that will result in a soil sample containing the contaminants of concern in the same proportion to the bulk matrix as it exists within the decision unit. Soil homogenization must be conducted following recommendations in DRDC TR 2011-447.

Requisite replicate and control samples will also be gathered. The soil sample analysis must be conducted by a SCC (Standards Council of Canada) and/or CALA (Canadian Association for Laboratory Accreditation) accredited laboratory. The list of organic environmental sampling constituents and breakdown products that need to be targeted in the sampling investigation are:

RDX, Tetryl, 1-3-5-Trinitrobenzene, 2-Amino-4-6-Dinitrotoluene (DNT), 4-Amino-2-6-DNT, 2-4-6-Trinitrotoluene (TNT), Nitrobenzene, 2-Nitrotoluene, 3-Nitrotoluene, 4-Nitrotoluene, 2-4-Dinitrotoluene, 2-6-Dinitrotoluene, Nitrobenzene.

The list of inorganic environmental sampling constituents that need to be targeted in the sampling investigation are:

Ag, Al, As, B, Ba, Be, Bi, Cd, Co, Cr, Cu, Fe, Hg, Li, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Te, Tl, Ti, U, V, Zn.

### **Soil Sampling Plan**

The Soil Sampling Plan shall contain the following:

- The sampling methodology and protocol.
- The proposed layout, location and size of decision units including the number of increments for soil collection.

- A map (or maps) showing the location and layout of each sampling decision unit.
- Estimated number of samples to be submitted to the laboratory for analysis.
- Sampling schedule.

### **Soil Sampling, Treatment and Analysis Report**

The report shall contain the following:

- The sampling methodology and protocol.
- Each sample must be identified by a unique identifier and include the date and time & the number of increments used.
- For each decision unit composite sample, the spatial location of the limits of the DU is to be provided in an appropriate coordinate system.
- The homogenization method used must be carefully described (either the acetone slurry or the grinding method).
- Field duplicates must be identified and standard deviation between replicates must be presented and discusses.
- The results for each sample of each contaminant, including non-detect values and analytical limits of detection.
- A map should be provided showing all decision unit soil sample locations.
- The results of the collected soil samples will be included as part of the project database and provided in digital format.

## List of symbols/abbreviations/acronyms/initialisms

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ADNT	Amino dinitrotoluene
2-A-DNT	2-Amino-4,6-dinitrotoluene
4-A-DNT	4-Amino-2,6-dinitrotoluene
AP	Ammonium perchlorate
ARET	Accelerated Reduction/Elimination of Toxics
BIP	Blow-in-place
BRI	Biotechnology Research Institute
°C	Degree Celcius
CAS	Chemical Abstract Service Registry
cc	Cubic centimetre
CCME	Canadian Council of Ministers of the Environment
CCV	Continuous calibration verification
CEC	Cation exchange capacity
CFRIS	Canadian Forces Range Inventory System
cm	Centimeter
CRREL	Cold Regions Research and Engineering Laboratory
d	Detection limit
DGE	Director General Environment
DLE	Director Land Environment
3,5-DNA	3,5-Dinitroaniline
1,3-DNB	1,3-Dinitrobenzene
DND	Department of National Defence
2,4-DNT	2,4-Dinitrotoluene
2,6-DNT	2,6-Dinitrotoluene
DoD	Department of Defense (U.S.)
DPA	Diphenylamine
DRDC	Defence Research and Development Canada
DRDKIM	Director Research and Development Knowledge and Information Management
EC	Ethyl centralite
ECOS	Environment Council of the States

EM	Energetic material
EOD	Explosive ordnance disposal
EPA	Environmental Protection Agency
FE	Fundamental error
FP	Firing position
g	Gram
GPS	Global positioning system
HE	High explosive
HMX	High melting explosive or octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
HPLC	High Pressure Liquid Chromatography
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
INRS-ETE	Institut national de la recherche scientifique – Eau, Terre et Environnement
ISQG	Industrial Soil Quality Guidelines
MC	Munition constituent
METC	Munitions Experimental Test Center
MHT	Maximum holding time
min	Minute
MISS	Multi-increment soil sample
ml	Milliliter
mm	Millimeter
NA	Not available
NATO	North Atlantic Treaty Organization
NB	Nitrobenzene
NC	Nitrocellulose
NG	Nitroglycerine
NQ	Nitroguanidine
2-NT	2-Nitrotoluene
3-NT	3- Nitrotoluene
4-NT	4- Nitrotoluene
PBX	Polymer bonded explosives
PE	Polyethylene
PETN	Pentaerythritol tetranitrate



ppm	Part per million (mg/kg)
QA	Quality assurance
QC	Quality control
RSD	Relative standard deviation
RDX	Research development explosive or 1,3,5-hexahydro-1,3,5-trinitrotriazine
R&D	Research & Development
RTA	Range and Training Area
sec	Second
SERDP	Strategic Environmental R&D Programme
SSL	Soil screening level
TAT	triaminotolunene
Tetryl	Methyl-2,4,6-trinitrophenylnitramine
1,3,5-TNB	1,3,5-Trinitrobenzene
TNT	2,4,6-Trinitrotoluene
TTCP	The Technical Cooperation Programme
U.S.	United States
µm	Micrometer
UV	Ultraviolet
UXO	Unexploded ordnance
v/v	Volume / volume

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This document represents a comprehensive site characterization guidance addressing the determination of the concentration of munitions constituents in military training range surface soils. It is based on more than 15 years of multidisciplinary research dedicated to the study of the source, dispersion, fate and transport of munitions constituents. Energetic residues and metals are heterogeneously distributed over military training ranges as particles of various sizes, shapes, and compositions. The sampling strategy was designed to address the compositional and distributional heterogeneities and to obtain representative mean soil concentrations in area where munitions constituents are expected, or decision units. The sample treatment, processing and analysis were also carefully studied and optimized. Most munitions constituents are deposited on the surface, with the highest measured concentrations at firing positions, near targets, at low-order or cracked UXO vicinity and where demolition activities are performed. This report summarizes the sampling strategies recommended for various types of ranges and covers the safety aspects related to sampling in UXO contaminated lands, the sampling equipment, sample processing and analysis. This protocol was developed during investigations on active ranges and primarily addresses potential surface source zones from which munitions residues could be migrating into surface and groundwater systems.

Ce document est un guide détaillé de caractérisation des secteurs d'entraînement militaire ayant pour but de déterminer la concentration des résidus de munitions dans les sols de surface. Il est basé sur plus de 15 années de recherche pluridisciplinaire consacrée à l'étude de la source, la dispersion, le sort et le transport des constituants de munitions. Les résidus énergétiques et les métaux sont dispersés de façon hétérogène dans les secteurs d'entraînement militaire sous forme de particules de différentes tailles, formes et compositions. Les stratégies d'échantillonnage ont été développées pour répondre à l'hétérogénéité compositionnelle et de distributionnelle et afin de déterminer les concentrations moyennes de résidus dans les sols, à l'intérieur d'unités de décisions, soient les zones où la présence de résidus de munitions est suspectée. Le traitement, la préparation et l'analyse de l'échantillon ont été soigneusement étudiés et optimisés. La plupart des constituants des munitions sont déposés sur la surface, avec les concentrations les plus élevées retrouvées aux positions de tir, autour des cibles, à proximité et autour des munitions non éclatées ou craquées et aussi là où les activités de démolition sont effectuées. Ce rapport résume les stratégies d'échantillonnage recommandées pour les différents types de champs de tir et couvre les aspects de sécurité liés à l'échantillonnage dans des terrains contenant des munitions non éclatées, le matériel d'échantillonnage, le traitement des échantillons ainsi que l'analyse. Ce protocole a été développé au cours de caractérisations effectuées sur les secteurs d'entraînement actifs et traite principalement des sources potentielles dans les zones de surface à partir desquelles les résidus de munitions pourraient migrer vers les systèmes d'eau de surface et d'eau souterraine.

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Range and training area; characterization; soil sampling strategies; composite; munition constituents; contamination; ammunition; sampling protocol; explosives; propellants; metals;



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